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SUPPORTING INFORMATION

# Poly(ferrocenylene iminoborane): an inorganic–organic hybrid polymer comprising a backbone of moderately interacting ferrocenes

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**Abstract:** The first poly(ferrocenylene iminoborane), that is, a polyferrocene-based metallopolymer featuring C=C-isoelectronic/-isosteric B=N linking units, and a series of monodisperse ferrocenylene iminoborane oligomers are presented. Our studies provide important insight into the structural and electronic nature of this novel class of hybrid materials.

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## Experimental Section

### General procedures.

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glovebox. Aqueous workup and purification by column chromatography were performed under air atmosphere. Solvents (DCM, diethyl ether, *n*-hexane, THF and toluene) were dried and degassed by means of an Innovative Technology solvent purification system (SPS). Deuterated solvents for NMR spectroscopy, *n*-pentane was dried and degassed at reflux over Na or $CaH_2$ ($CDCl_3$, $CD_2Cl_2$) and freshly distilled prior to use. Chlorotrimethylsilane ($Me_3SiCl$), *ortho*-difluorobenzene and *N*,*N*-dimethyltrimethylsilylamines ($Me_3SiNMe_2$) were purchased from commercial sources and were freshly distilled prior to use. Dibromoborylferrocene[1], 2,4,6-trimethylphenyllithium (MesLi)[2], *N*-ferrocenyl-*N*-dimethylsilylamine (**1**)[3], 1,1`-bis[(trimethylsilyl)amino]ferrocene (**4**)[4], and 1,1-´bis[bromo(mesityl)boryl]ferrocene (**3**)[5] were synthesized according to procedures described in literature.

Mass spectroscopy was performed on a Thermo Scientific Exactive Plus Orbitrap MS system, by atmospheric pressure chemical ionization (APCI), MALDI-TOF[6] measurement was performed on a Bruker Daltronics UltrafleXtreme. Analyzer in reflective (+) mode with delayed extraction. Benzo[a]pyrene was used as the matrix (5mg/500 ml toluene). The sample was prepared in toluene (2 mg/200 ml), mixed with the matrix in a 1:10 ratio, and then spotted on the wells of a sample plate inside a glove box. Peptides were used for calibration. Bruker Peptide Calibration Standard (Bruker Part No. 8206195) Angiotensin II (1046.5418), Angiotensin I (1296.6853), Substance P (1347.7354), Bombesin (1619.8223) ACTH clip 1-17 (2093.0867), ACTH clip 18-39 (2465.1989), Somatostatin 28 (3147.4710) with α-Cyano-4-hydroxycinnamic acid (HCCA – Bruker Part No. 8201344) as the matrix.

Elemental analyses were performed on an Elementar vario MICRO cube elemental analyzer.

NMR spectra were recorded at 25 °C on a BrukerAvance III HD spectrometer operating at 300 MHz, on a Bruker Avance 500 spectrometer operating at 500 MHz or on a Avance Neo I 600 operating at 600 MHz. Chemical shifts were referenced to residual protic impurities in the solvent ($^1H$) or the deuterated solvent itself ($^{13}C$) and reported relative to external $SiMe_4$ ($^1H$, $^{13}C$) or $BF_3{\cdot}OEt_2$ ($^{11}B$) standards.

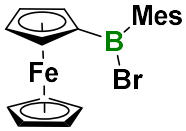
Crystals suitable for single crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-Kα radiation. The crystal data of **7** was collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated Mo-Kα radiation. The crystals were cooled using an Oxford Cryostreams low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)[7] and Fourier expansion technique. All non-hydrogen at-oms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F2 of all data, using SHELXL[8] software and the SHELXLE graphical user interface.[9]

Analytical GPC chromatograms were recorded on an Agilent 1260 Infinity II Series GPC equipped with a PSS DSV 3 µm precolumn, two PSS SDV 3 µm 1000 Å columns and one PSS SDV 3 µm 10000 Å in series. All measurements were taken in THF at 298 K with a flow rate of 1 mL/min and toluene as internal standard (calibrated against polystyrene standards). Three different detectors were applied for observation. Two variable wavelength detectors (VWD 1 and 2) and a refraction index detector (RID). Evaluation of the chromatograms was performed by using WinGPC software.

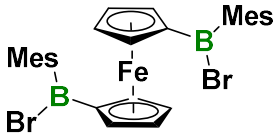
The cyclic voltammograms were measured with a PGSTAT30 potentiostat from Metrohm Autolab in a measuring cell with a three-electrode setup under an argon atmosphere. The evaluation was performed using the Nova 2.0 software. An ESA EE047 glassy-carbon electrode in glass with an inner diameter of 3 mm, an outer diameter of 6 mm and an electrode area of 7.1 $mm^2$ served as the working electrode. A RE-7 nonaqueous reference electrode ($Ag/Ag^+$) made of Vycorglass filled with a 0.1 mol/L

[*n*-$Bu_4N$][$PF_6$]/0.01 mol/L $AgNO_3$-THF solution and a silver wire was used as the reference electrode. A platinum wire with a length of 5 cm and a diameter of 0.5 mm and an area of 78.7 $mm^2$ was used as a counter electrode. The investigated compounds were measured in a 0.1 mol/L [*n*-$Bu_4N$][$PF_6$] THF solution with a sample concentration of $1 \cdot 10^{-3}$ mol/L. The scans were referenced after the addition of a small amount of decamethylferrocene (bis(pentamethylcyclopentadienyl)iron(II)) as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple.

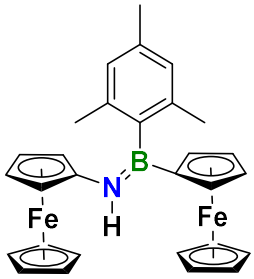
## Syntheses



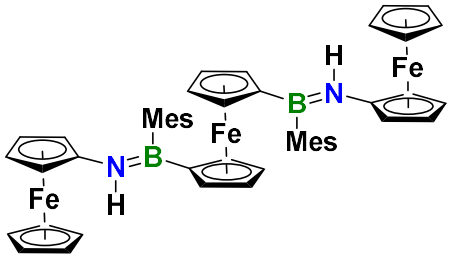

**Synthesis of 2.** To a stirred solution of (dibromoboryl)ferrocene (4.27 g, 12.0 mmol) in *n*-hexane (100 mL) was added a suspension of MesLi (1.59 g, 12.6 mmol) in toluene (40 mL) at −78 °C. Subsequently, the mixture was warmed to room temperature and stirred overnight. The solid was filtered off and all volatiles were removed *in vacuo*. The crude product was crystallized from a mixture of DCM/*n*-hexane (1/3) at −30 °C. **2** was obtained as a red solid. **Yield**: 3.88 g (9.82 mmol, 82%); **$^{1}$H NMR** (500 MHz, $CDCl_3$): δ = 6.85 (m, 2H; *m*-Mes-C*H*), 4.77 (br t, 2H, *J* = 1.79 Hz, Cp-C*H*), 4.50 (br t, 2H, *J* = 1.81 Hz Cp-C*H*), 4.27 (s, 5H, Cp-C*H*), 2.35 (s, 6H, *o*-Mes-C$H_3$), 2.32 (s, 3H, *p*-Mes-C$H_3$) ppm; **$^{11}$B{$^{1}$H} NMR** (96 MHz, $CDCl_3$): δ = 66.8 ppm; **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$): δ = 139.2 (br, $C_{ipso}$-Mes-B) 138.7 (s, *p*-C-Mes), 138.3 (s, *o*-C-Mes), 127.9 (s, *m*-C-Mes), 76.8 (s, Cp), 75.8 (s, Cp), 70.0 (s, Cp), 23.0 (s, *o*-Mes-$CH_3$), 21.3 (s, *p*-Mes-$CH_3$); not observed ($C_{ipso}$-Cp) ppm. **HRMS** (LIFDI) m/z calcd. for $C_{19}H_{20}BBrFe$: 394.0185; found 394.0177 [$M^+$].



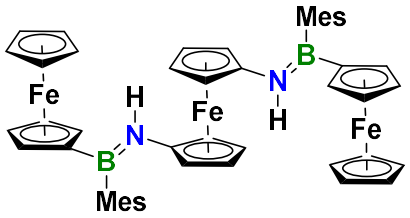

**Synthesis of 3.** To a stirred solution of 1,1'-bis(dibromoboryl)ferrocene (7.88 g, 15.0 mmol) in *n*-hexane (100 mL) was added a suspension of MesLi (3.97 g, 31.5 mmol) in toluene (60 mL) at −78 °C. Subsequently, the mixture was warmed to room temperature and stirred overnight. The solid was filtered off and all volatiles were removed *in vacuo*. The crude product was crystallized from a mixture of DCM/*n*-hexane. **3** was obtained as a red solid. **Yield**: 7.19 g (11.9 mmol, 79%); **$^{1}$H NMR** (600 MHz, $CDCl_3$): δ = 6.83(s, 4H; *m*-$Ar_{Mes}$-*H*), 4.88(t, 4H, *J* = 1.89 Hz, Cp-*H*), 4.59 (br t, 4H; *J* = 1.83 Hz Cp-*H*), 2.33(s, 6H, *p*-Mes-C$H_3$), 2.27(s, 12H, *o*-Mes-C$H_3$) ppm; **$^{11}$B{$^{1}$H} NMR** (193 MHz, $CDCl_3$): d = 67.7ppm (s); **$^{13}$C{$^{1}$H} NMR** (151 MHz $CDCl_3$): d = 139.0 (s, C-*p*-Mes), 138.7 (s, *ipso*-C-$Ar_{Mes}$-B), 138.3 (s, C-*o*-Mes), 128.1 (s, C-*m*-Mes), 77.7(s, Cp), 77.4(s, Cp), 76.8 (s, *ipso*-Cp-B), 23.0 (s, *o*-Mes-*C*$H_3$), 21.4 (s, *p*-Mes-*C*$H_3$) ppm. **HRMS** (LIFDI) m/z calcd. for $C_{28}H_{30}B_2Br_2Fe$: 604.0224; found 604.0229 [$M^+$].



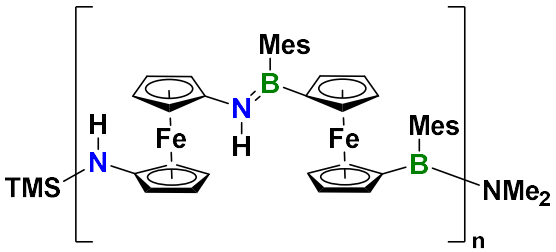

**Synthesis of 5.** To a solution of bromo(mesityl)(ferrocenyl)borane **2** (99.0 mg, 0.25 mmol) in DCM (0.5 mL) a solution of [(trimethylsilyl)amino]ferrocene **1** (68.0 mg, 0.25 mmol) in DCM (1 mL) was added and stirred for 16 h at room temperature. All volatiles were removed *in vacuo*, to afford the product as a dark yellow solid. **Yield**: 105 mg (0.20 mmol, 80 %); **$^{1}$H NMR** (500 MHz, $CDCl_3$): δ = 6.81 (s, 2H, *m*-Mes-C*H*), 5.70 (s, 1H, N-*H*), 4.37 (s, 2H, B-Cp-C*H*), 4.18 (s, 2H, B-Cp-C*H*), 4.15 (s, 5H, B-Cp-C*H*), 4.10 (s, 5H, N-Cp-C*H*), 3.87-3.84 (m, 4H, N-Cp-C*H*), 2.32 (s, 3H, *p*-Mes-C$H_3$), 2.23 (s, 6H, *o*-Mes-C$H_3$) ppm; **$^{11}$B{$^{1}$H} NMR** (193 MHz, $CDCl_3$): δ = 43.7 ppm; **$^{13}$C{$^{1}$H} NMR** (151 MHz, $CDCl_3$): δ = 138.5 (s, *o*-Mes-$C_q$), 136.8 (s, *p*-Mes-$C_q$), 127.1 (s, *m*-Mes-*C*H), 72.9 (s, B-Cp-*C*H), 71.3 (s, B-Cp-*C*H), 69.4 (s, N-Cp-*C*H), 68.7 (s, B-Cp-*C*H), 64.3 (s, N-Cp-*C*H), 60.4 (s, N-Cp-*C*H), 22.4 (s, *o*-Mes-*C*$H_3$), 21.4 (s, *p*-Mes-*C*$H_3$ ) ppm. (B-$C_{ipso}$-Cp and N-$C_{ipso}$-Cp were not observed); **HRMS**: (APCI pos) m/z calcd. for $C_{29}H_{30}BFe_2N$ + H: 516.1243, found: 516.1220 [M+H]$^+$; **Elem. anal.**: calc. (%): C 67.63, H 5.87, N 2.72; found: C 66.31, H 5.93, N 2.81.




**Synthesis of 6.** To a solution of 1,1´-bis[bromo(2,4,6-trimethylphenyl)boryl]ferrocene **3** (152 mg, 0.25 mmol) in DCM (2 mL) a solution of **1** (136 mg, 0.50 mmol) in DCM (1 mL) was added and stirred for 48 h at room temperature. All volatiles were removed *in vacuo*, to afford the product as a dark yellow solid. **Yield:** 190 mg (0.23 mmol, 46 %); **$^{1}$H NMR** (500 MHz, $CDCl_3$): δ = 6.85 (s, 4H, *m*-Mes-C*H*), 5.64 (s, 2H, N-*H*), 4.36 (s, 4H, N-Cp-C*H*), 4.15 (s, 4H, N-Cp-C*H*), 4.10 (s, 10H, N-Cp-C*H*), 3.84 (s, 8H, B-Cp-C*H*), 2.35 (s, 6H, *p*-Mes-C$H_3$), 2.24 (s, 12H, *o*-Mes-C$H_3$) ppm; **$^{11}$B{$^{1}$H} NMR** (160 MHz, $CDCl_3$): δ = 43.6 ppm; **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$): δ = 138.6 (*o*-Mes-$C_q$-$CH_3$), 137.0 (*p*-Mes-$C_q$-$CH_3$), 127.3 (*m*-Mes-*C*H), 73.9 (B-$C_{ipso}$-Cp), 73.2 (Cp-*C*H), 72.4 (Cp-*C*H), 69.5 (Cp-*C*H), 64.4 (Cp-*C*H), 60.5 (Cp-*C*H), 22.5 (*o*-Mes-*C*$H_3$), 21.5 (*p*-Mes-*C*$H_3$) ppm; **HRMS**: (APCI pos) m/z calcd. for $C_{48}H_{50}B_2Fe_3N_2$ + H: 845.2281, found: 845.2260 $[M+H]^+$; **Elem. anal.**: calc. (%): C 68.30, H 5.97, N 3.32; found: C 68.18, H 6.20, N 3.41.




**Synthesis of 7.** To a solution of **2** (198 mg, 0.50 mmol) in DCM (2 mL) a solution of **4** (90.0 mg, 0.25 mmol) in DCM (1 mL) was added and stirred for 48 h at room temperature. All volatiles were removed *in vacuo*, giving an orange solid. It was crystallized in *n*-hexane (4 mL) and DCM (4 mL) at -30 °C. The crystals were filtrated and dried *in vacuo*, to afford the product as a dark orange powder. **Yield:** 82 mg (97.0 µmol, 44 %); **$^{1}$H NMR** (500 MHz, $CDCl_3$): δ = 6.82 (s, 4H, *m*-Mes-C*H*), 5.66 (m, 2H, N-*H*), 4.34 (s, 4H, B-Cp-C*H*), 4.28 (m, 2H, Cp-C*H*), 4.11 (s, 10H, Cp-C*H*), 4.06 (m, 2H, Cp-C*H*), 4.02 (m, 2H, Cp-C*H*), 3.87 (m, 2H, Cp-C*H*), 3.77 (m, 4H, Cp-C*H*), 2.33 (s, 6H, *p*-Mes-C$H_3$), 2.21 (s, 12H, *o*-Mes-C$H_3$) ppm; **$^{11}$B{$^{1}$H} NMR** (160 MHz, $CDCl_3$): δ = 43.4 ppm; **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$): δ = 138.6 (*o*-Mes-$C_q$-$CH_3$), 136.8 (*p*-Mes-$C_q$-$CH_3$), 127.2 (*m*-Mes-*C*H), 101.9 (N-$C_{ipso}$-Cp), 98.80 (s, N-$C_{ipso}$-Cp), 73.5 (B-$C_{ipso}$-Cp), 72.9 (B-Cp-*C*H), 71.3 (B-Cp-*C*H), 68.7 (Cp-*C*H), 68.6 (N-Cp-*C*H), 66.5 (N-Cp-*C*H), 61.5 (N-Cp-*C*H), 22.5 (*o*-Mes-*C*$H_3$), 21.4 (*p*-Mes-*C*$H_3$) ppm; **HRMS**: (APCI pos) m/z calcd. for $C_{48}H_{50}B_2Fe_3N_2$ + H: 845.2281, found: 845.2257 $[M+H]^+$; **Elem. anal.**: calc. (%): C 68.30, H 5.97, N 3.32; found: C 68.91, H 5.74, N 3.36.




**Synthesis of 8.** To a solution of **3** (60.4 mg), 0.10 mmol) in DCM (0.5 mL) a solution of **4** (36.0 mg, 0.10 mmol) in DCM (0.5 mL) was added. It was stirred at room temperature for 14 days. $TMSNMe_2$ (11 mg, 0.09 mmol) was added, and the reaction mixture stirred for another 2 hours. Then it was injected in cold *n*-pentane (7 mL), filtered off and the residue washed with cold *n*-pentane

(3x2 mL). The solid was dried *in vacuo*, to afford the product as an orange powder. **Yield**: 52 mg (67.0 µmol, 67 %); **$^{1}$H NMR** (500 MHz, $CDCl_3$): δ = 6.81 (s, 4H, *m*-Mes-C*H*), 5.56 (s, 2H, N-H), 4.25 (s, 4H, Cp-C*H*), 4.03 (s, 4H, Cp-C*H*), 3.65 (m, 8H, Cp-C*H*), 2.33 (s, 6H, *p*-Mes-C$H_3$), 2.15 (s, 12H, *o*-Mes-C$H_3$) ppm; **$^{11}$B{$^{1}$H} NMR** (160 MHz, $CDCl_3$): δ = 43.4 ppm; **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CDCl_3$): δ = 138.6 (*o*-Mes-$C_q$-$CH_3$), 136.9 (*p*-Mes-$C_q$-$CH_3$), 127.3 (*m*-Mes-*C*H), 101.4 (N-$C_{ipso}$-Cp), 73.6 (B-$C_{ipso}$-Cp), 73.2 (B-Cp-*C*H), 72.3 (B-Cp-*C*H), 66.2 (N-Cp-*C*H), 61.4 (N-Cp-*C*H), 22.6 (*o*-Mes-*C*$H_3$), 22.5 (*p*-Mes-*C*$H_3$) ppm.

## NMR spectra

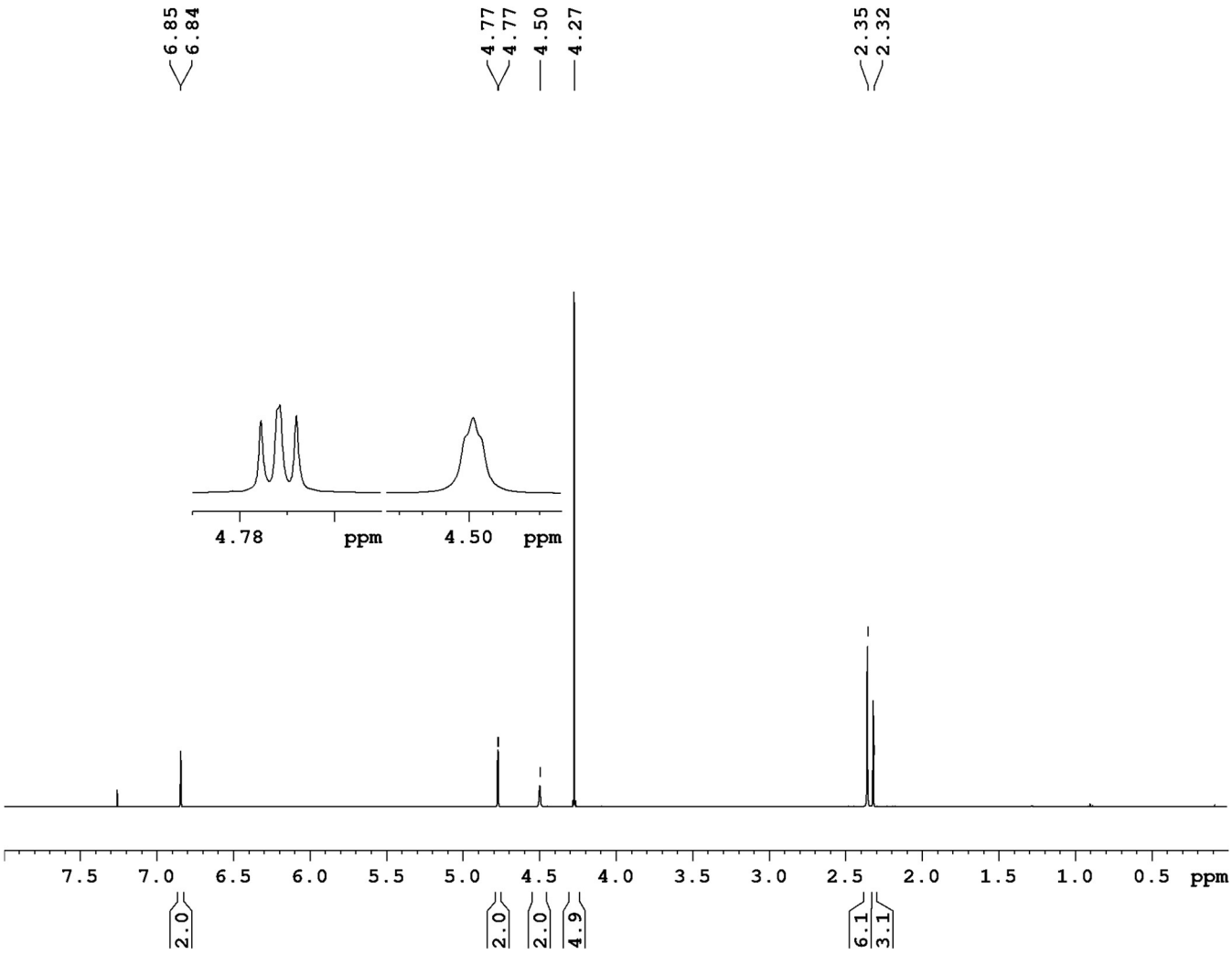



**Figure 1.** $^{1}H$ NMR spectrum of **2** (500 MHz, $CDCl_3$).

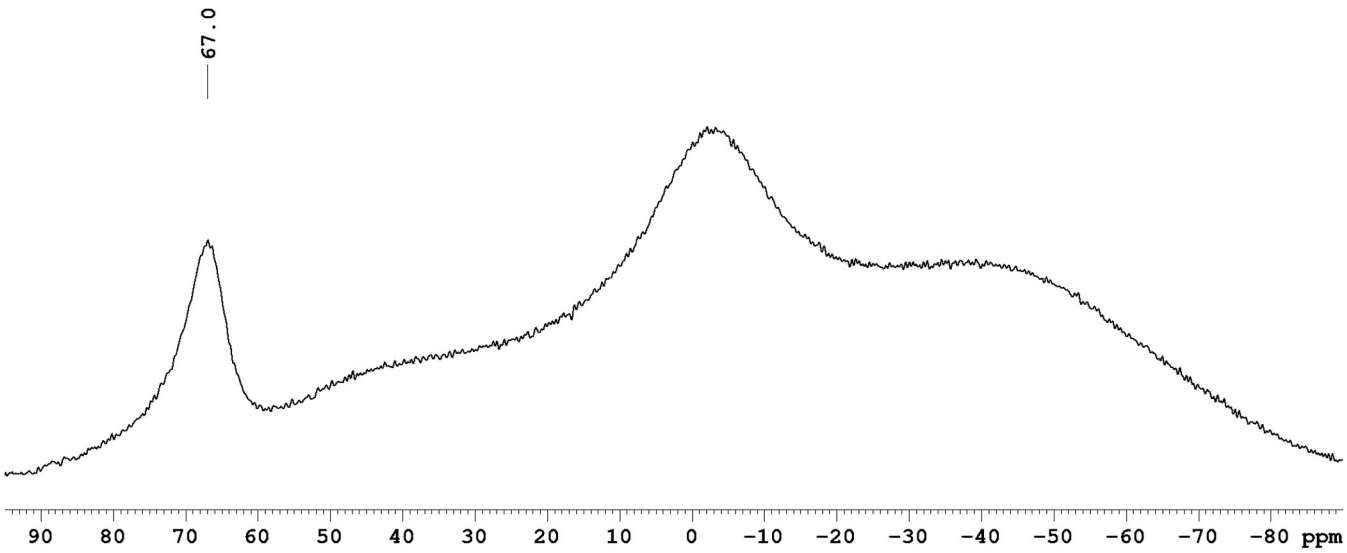



**Figure 2.** $^{11}B\{^{1}H\}$ NMR spectrum of **2** (96 MHz, $CDCl_3$).

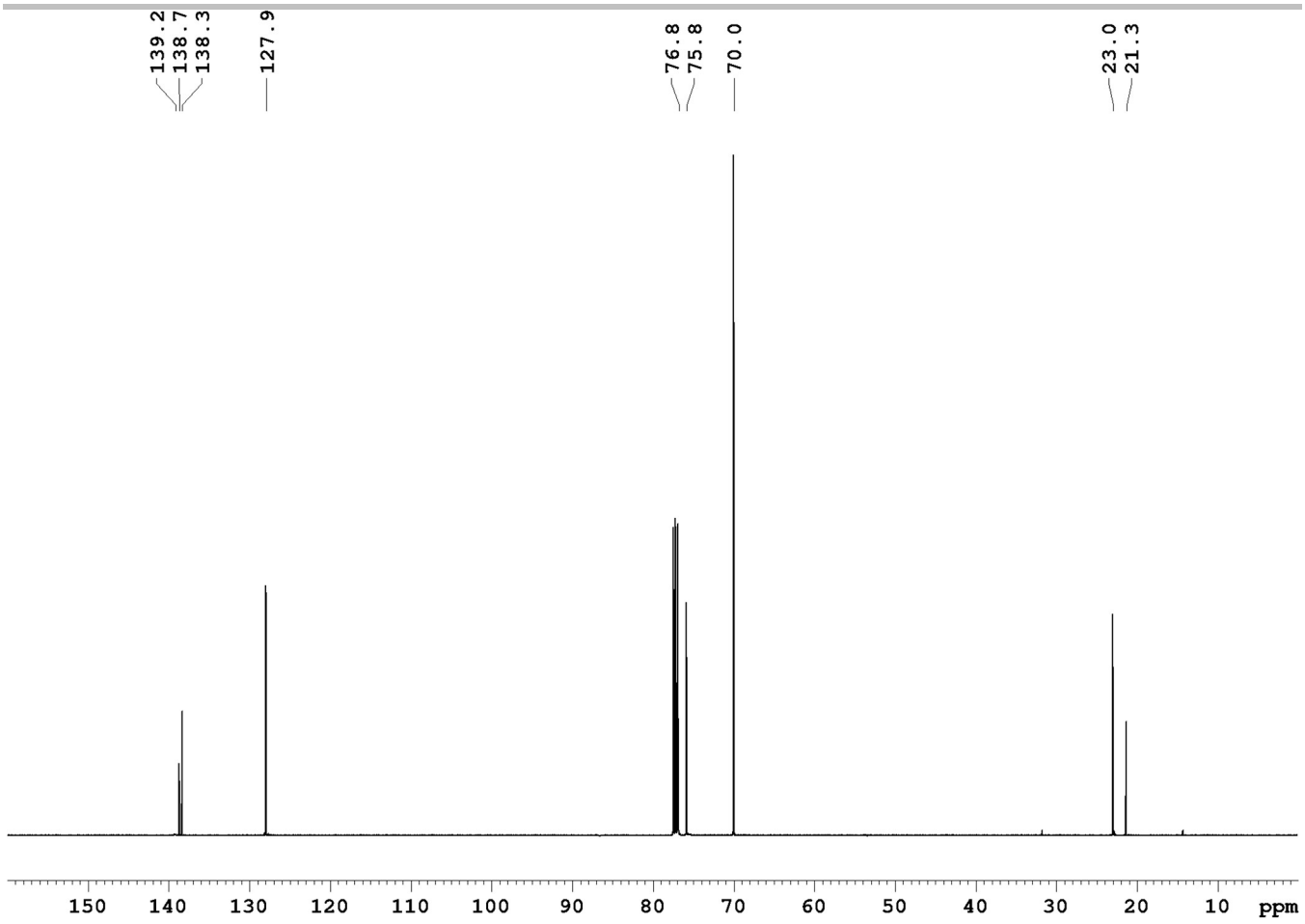



**Figure 3.** $^{13}C$ NMR spectrum of **2** (125 MHz, $CDCl_3$).

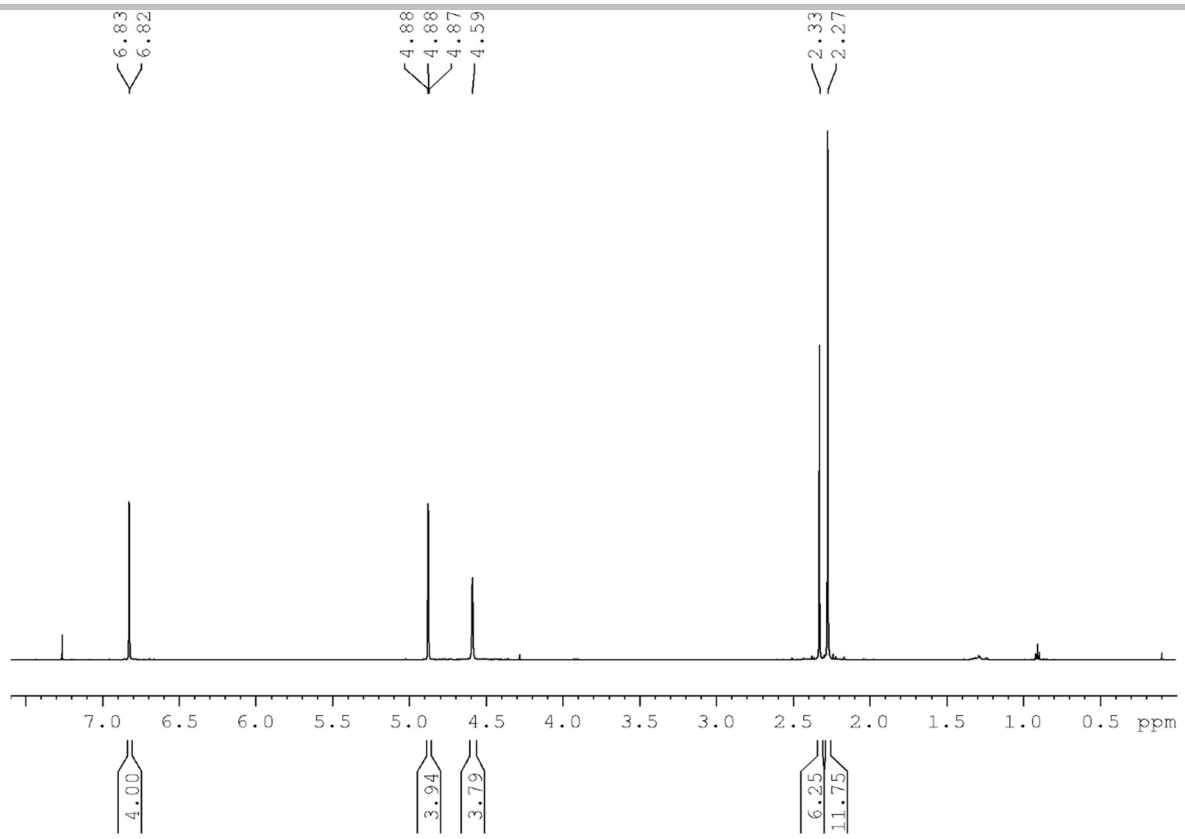



**Figure 4.** $^{1}H$ NMR spectrum of **3** (500 MHz, $CDCl_3$).

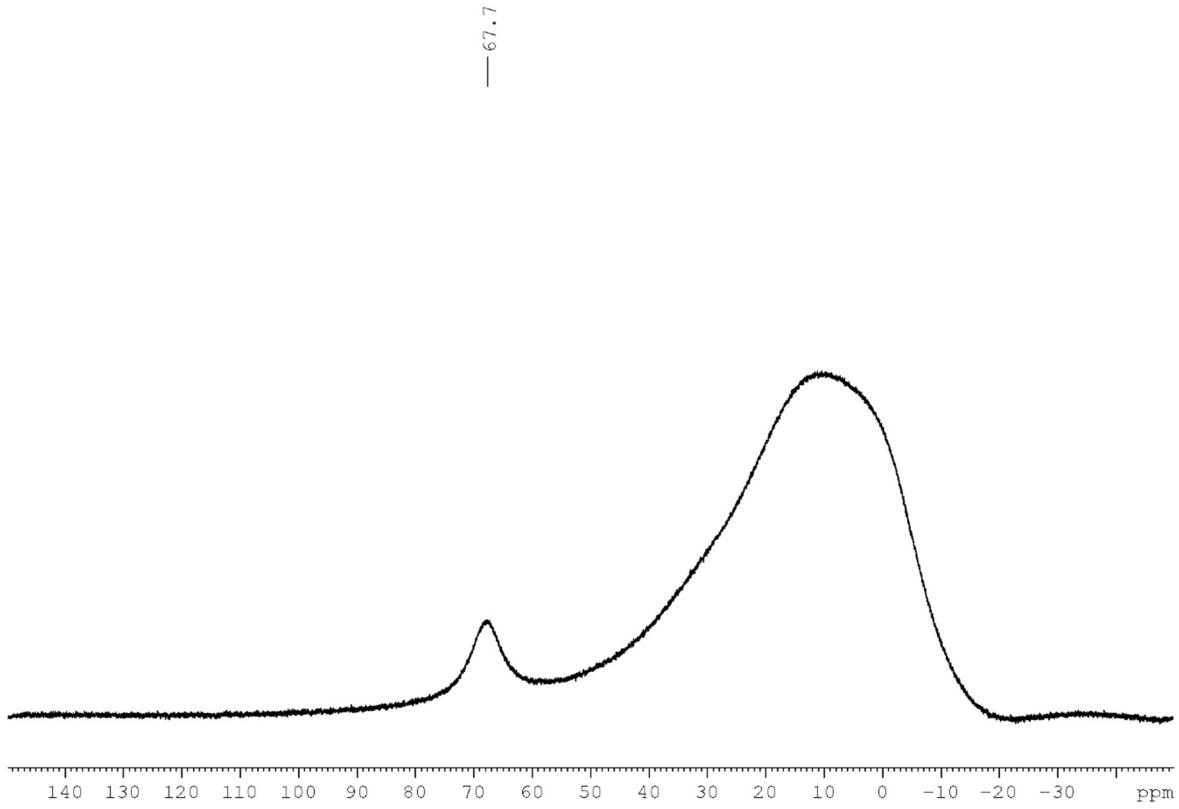



**Figure 5.** $^{11}B\{^{1}H\}$ NMR spectrum of **3** (96 MHz, $CDCl_3$).

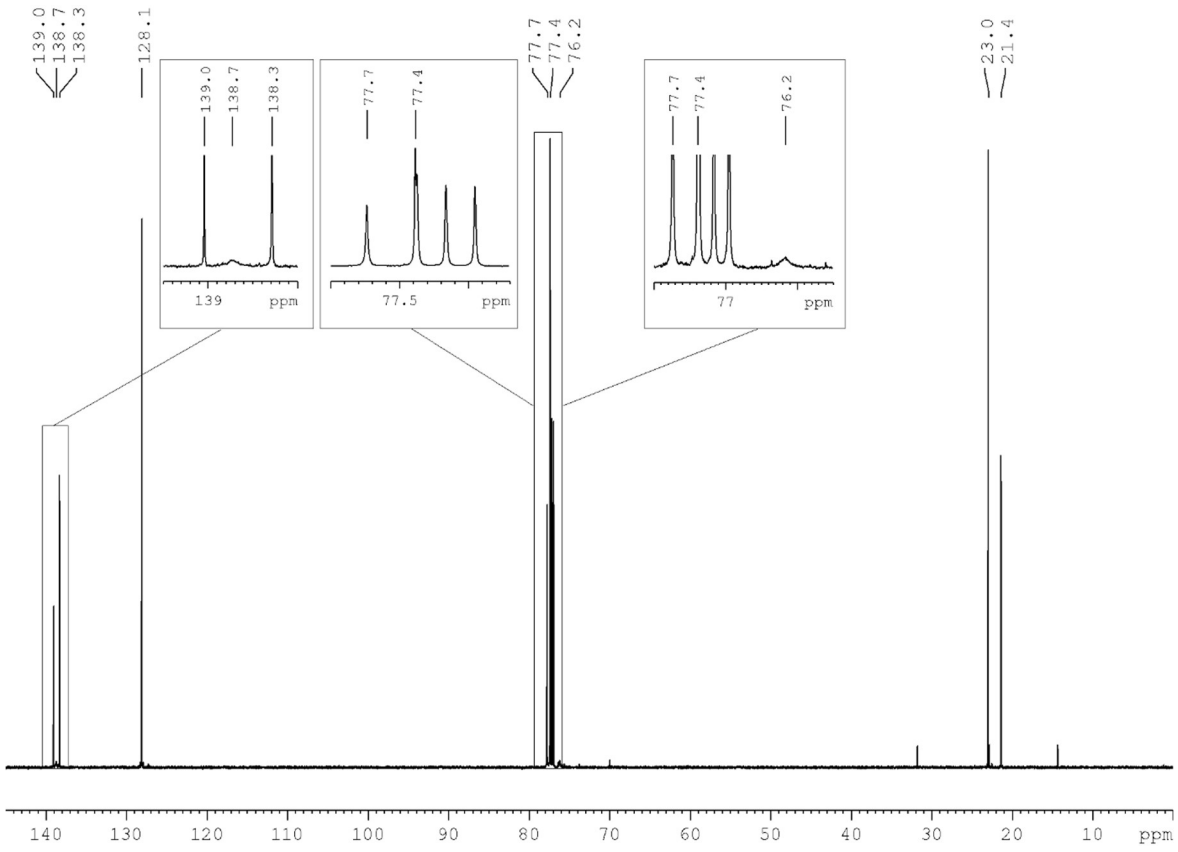



**Figure 6.** $^{13}C$ NMR spectrum of **3** (125 MHz, $CDCl_3$).

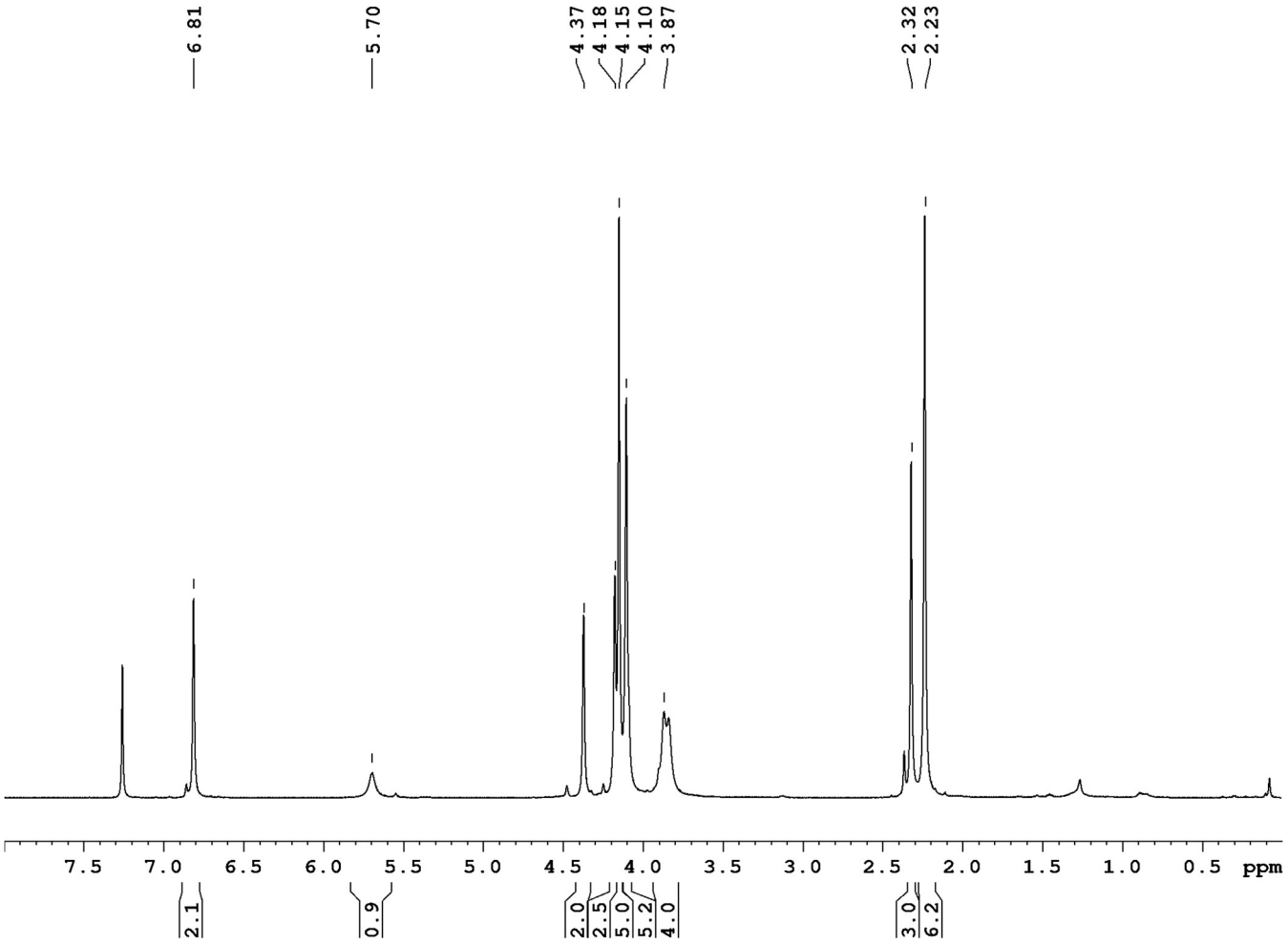



**Figure 7.** $^{1}H$ NMR spectrum of **5** (500 MHz, $CDCl_3$).

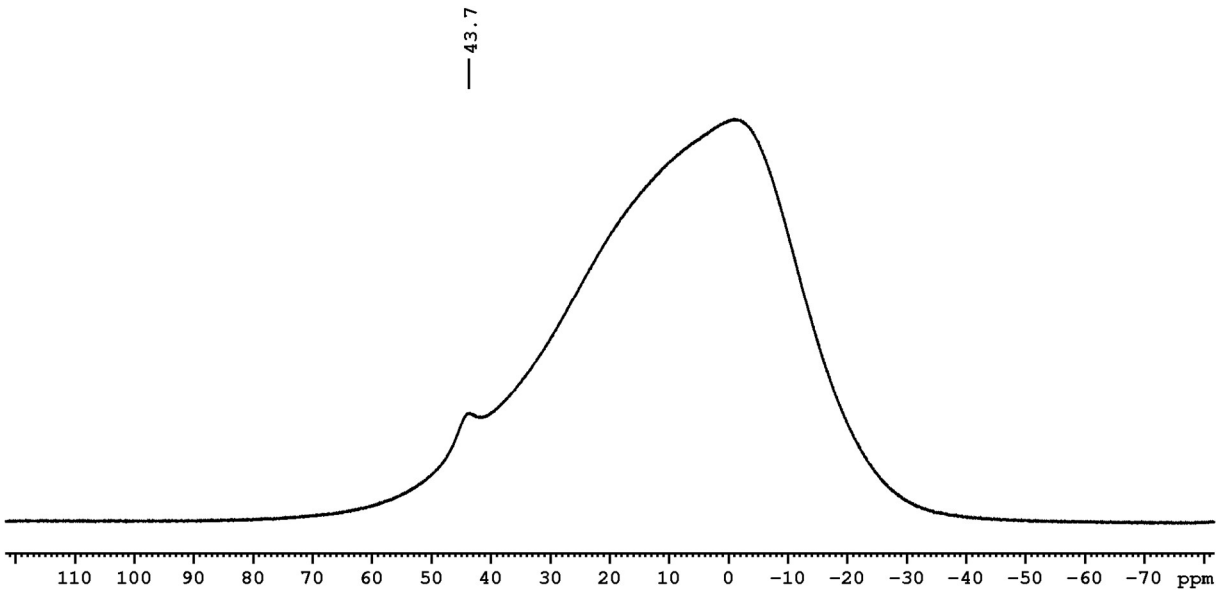



**Figure 8.** $^{11}B\{^{1}H\}$ NMR spectrum of **5** (160 MHz, $CDCl_3$).

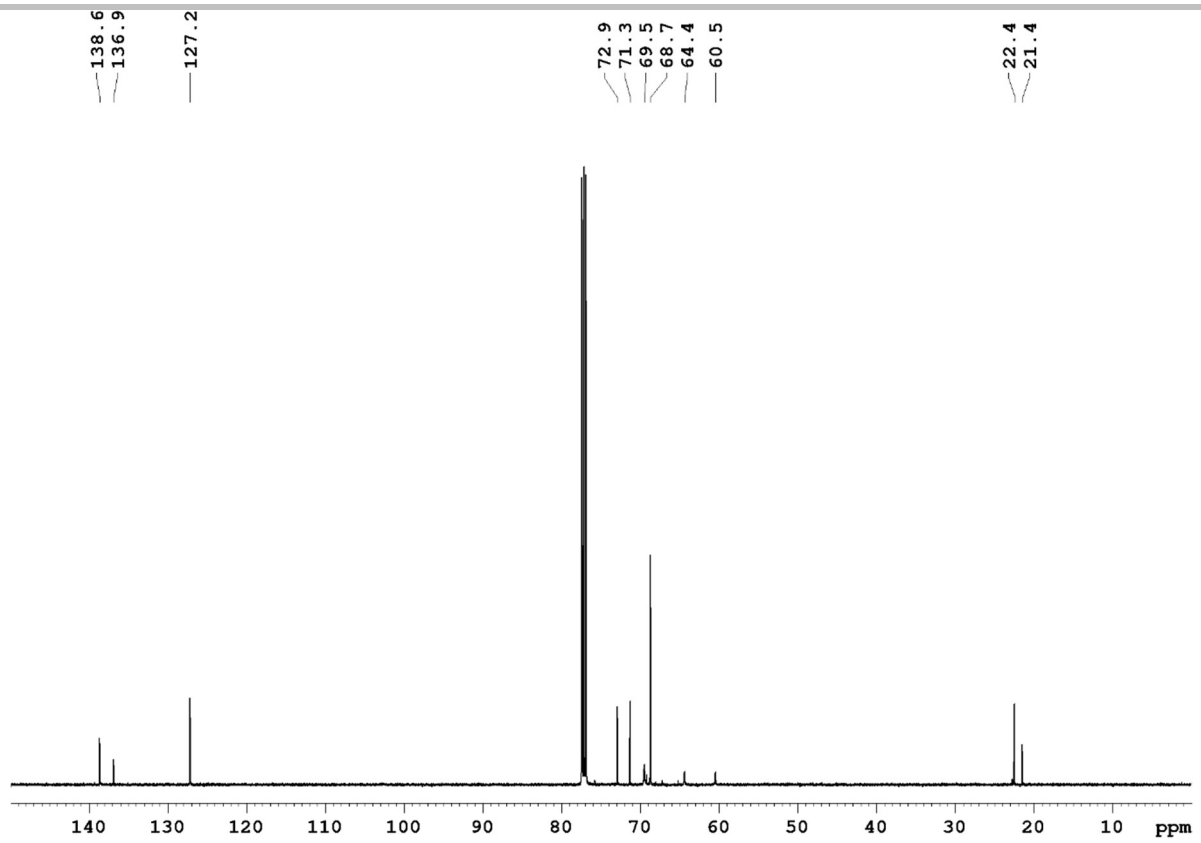



**Figure 9.** $^{13}C$ NMR spectrum of **5** (125 MHz, $CDCl_3$).

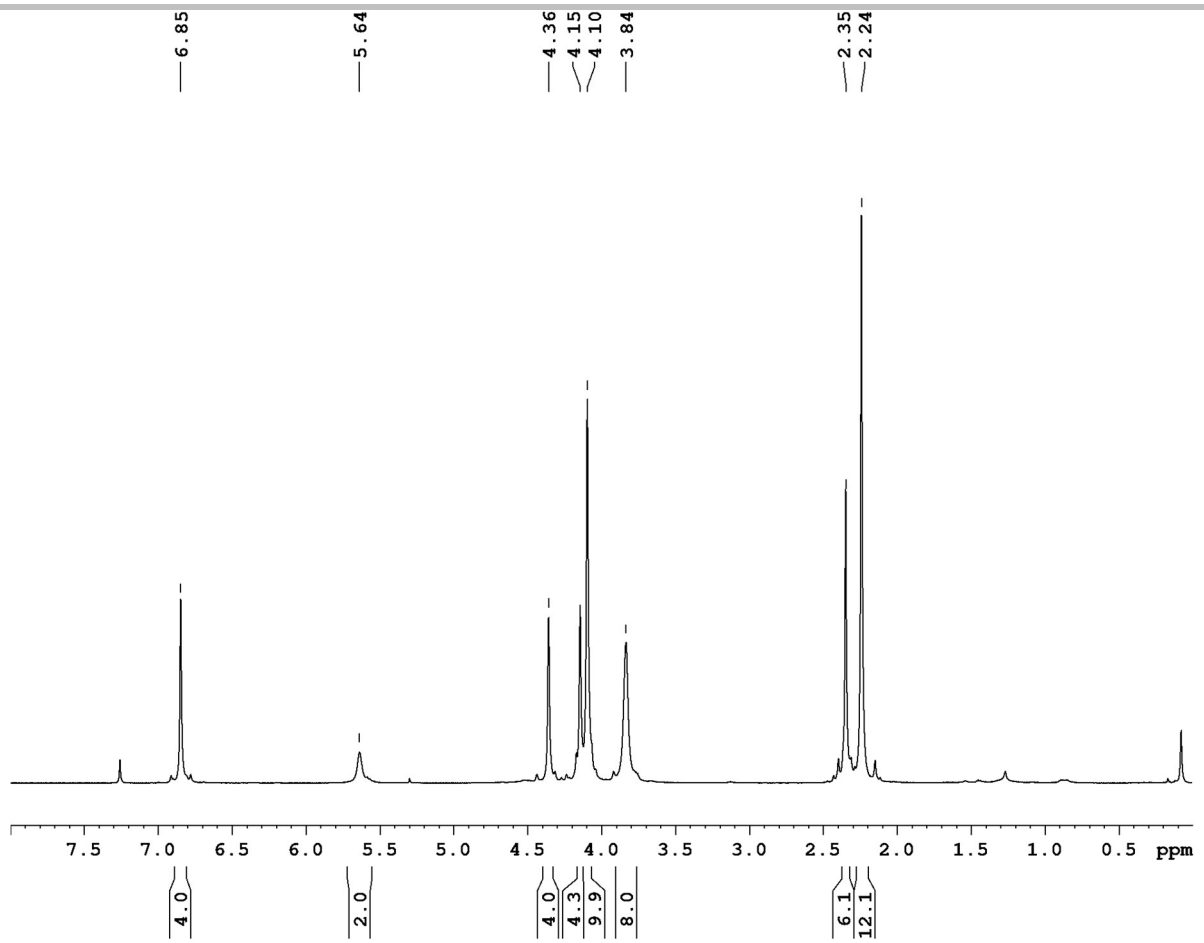



**Figure 10.** $^{1}H$ NMR spectrum of **6** (500 MHz, $CDCl_3$).

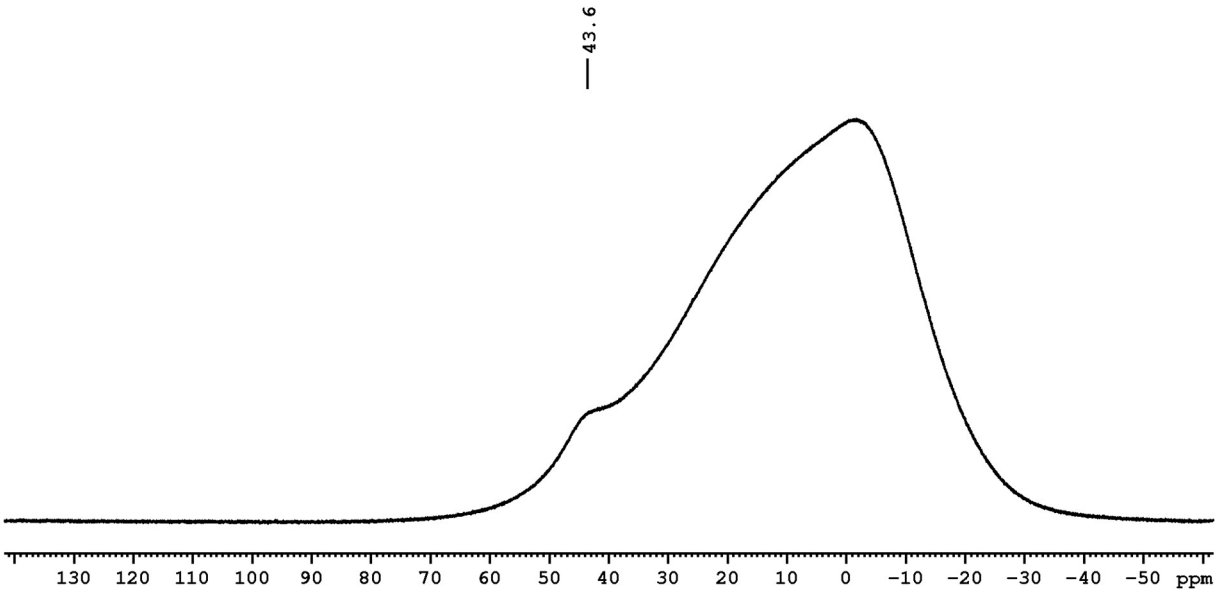



**Figure 11.** $^{11}B\{^{1}H\}$ NMR spectrum of **6** (160 MHz, $CDCl_3$).

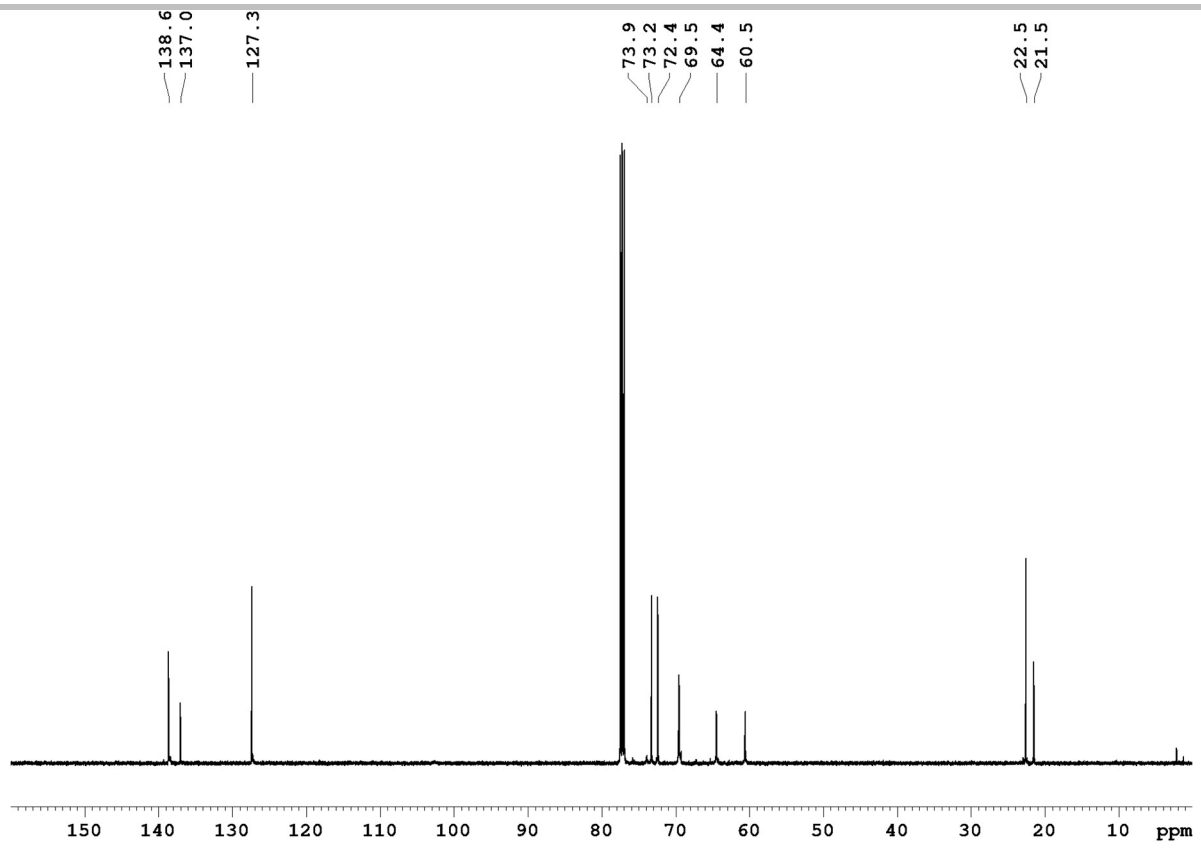



**Figure 12.** $^{13}C$ NMR spectrum of **6** (126 MHz, $CDCl_3$).

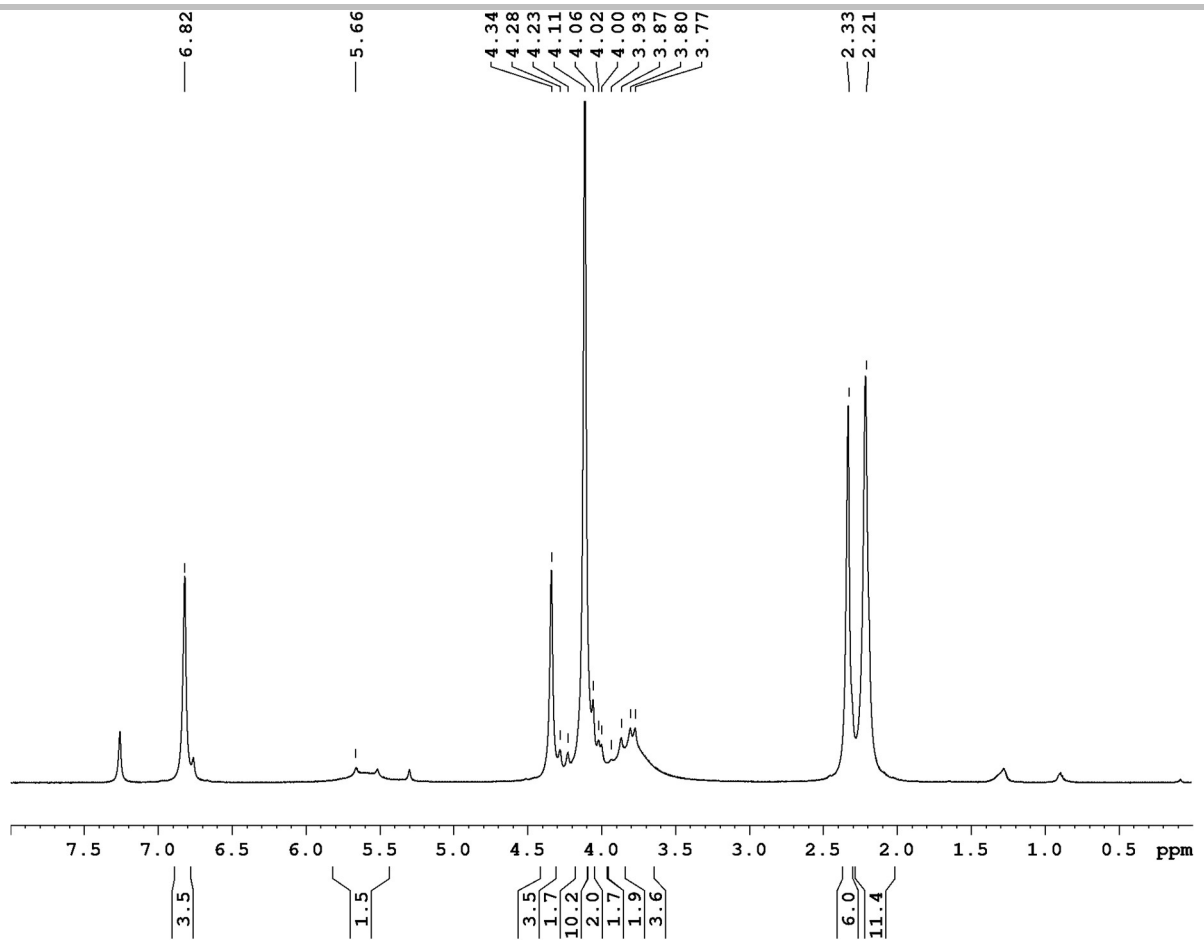



**Figure 13.** $^{1}H$ NMR spectrum of **7** (500 MHz, $CDCl_3$).

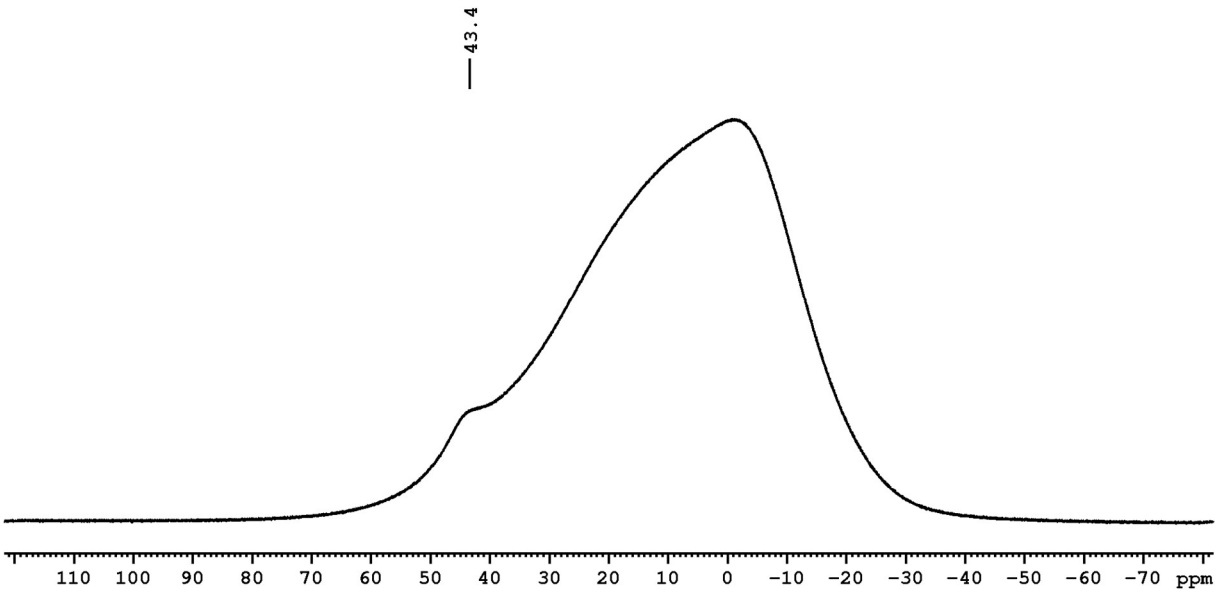



**Figure 14.** $^{11}B\{^{1}H\}$ NMR spectrum of **7** (160 MHz, $CDCl_3$).

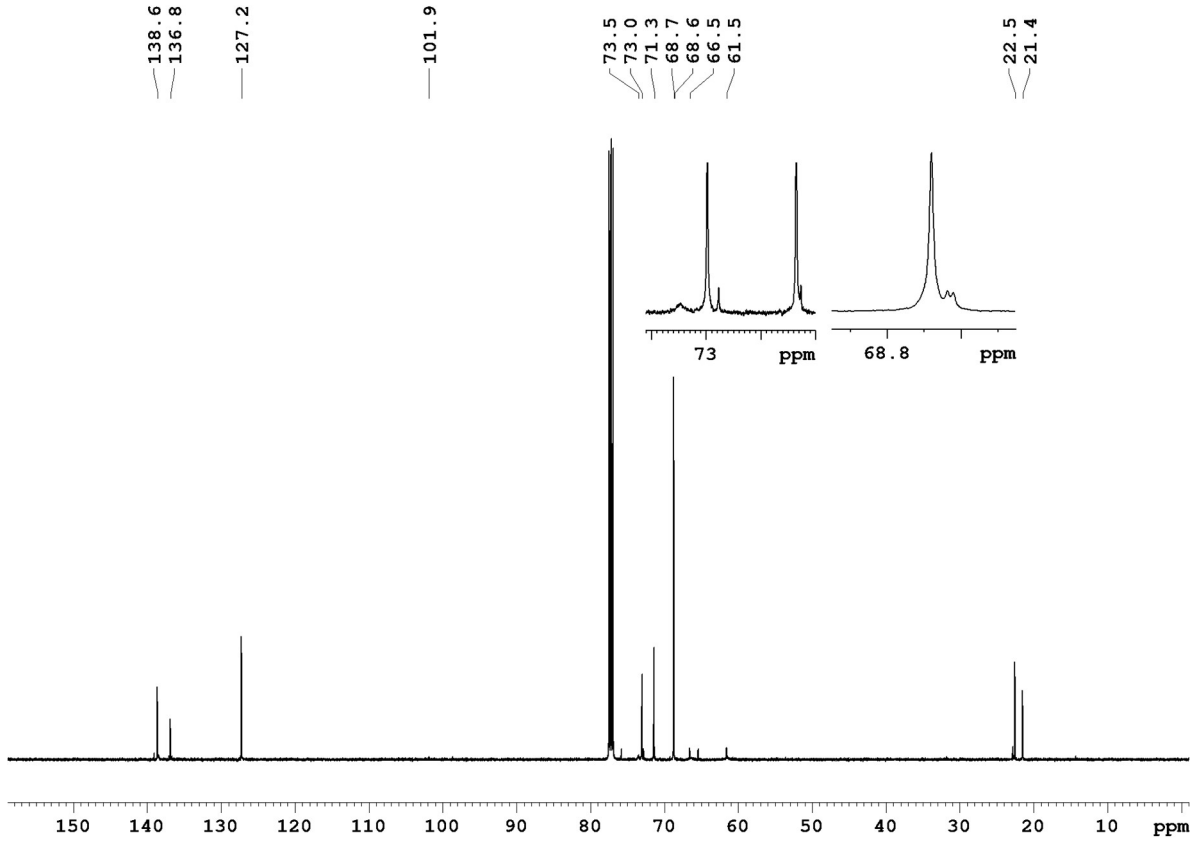



**Figure 15.** $^{13}C$ NMR spectrum of **7** (126 MHz, $CDCl_3$).

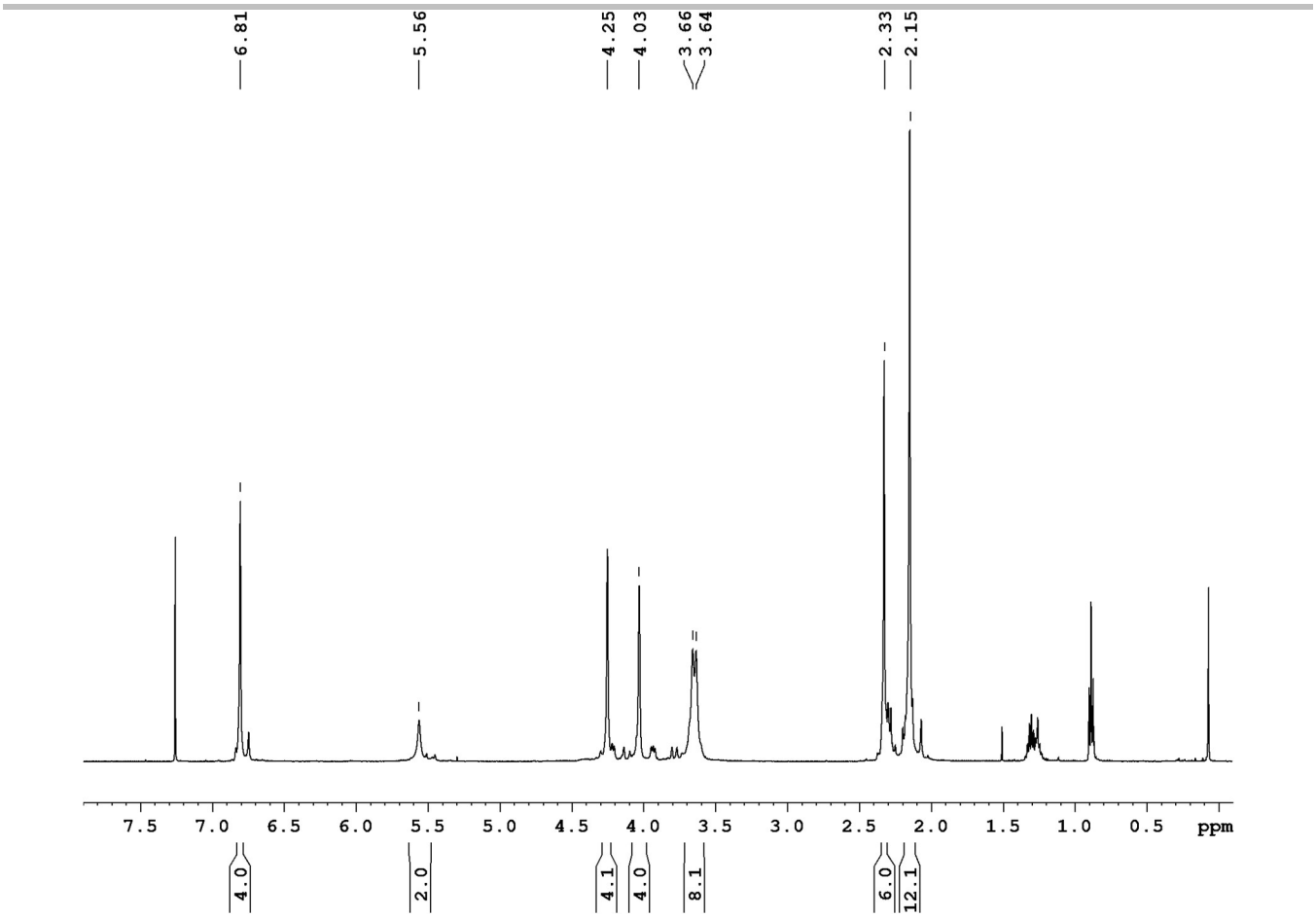



**Figure 16.** $^{1}H$ NMR spectrum of **8** (500 MHz, $CDCl_3$).

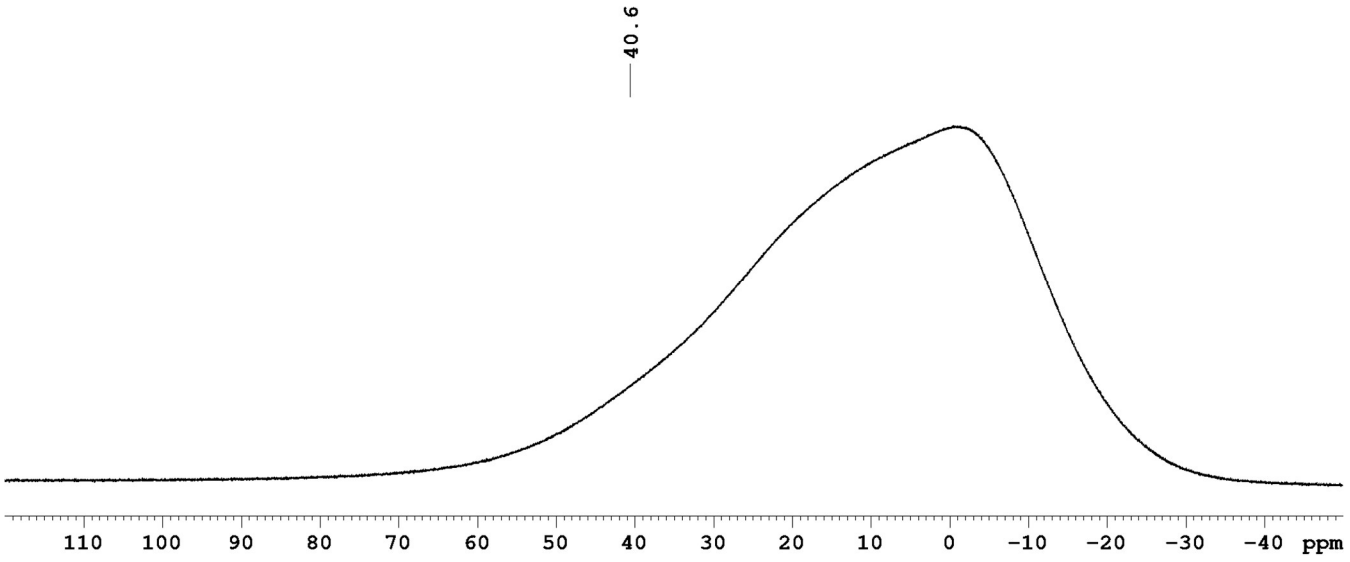



**Figure 17.** $^{11}B\{^{1}H\}$ NMR spectrum of **8** (160 MHz, $CDCl_3$).

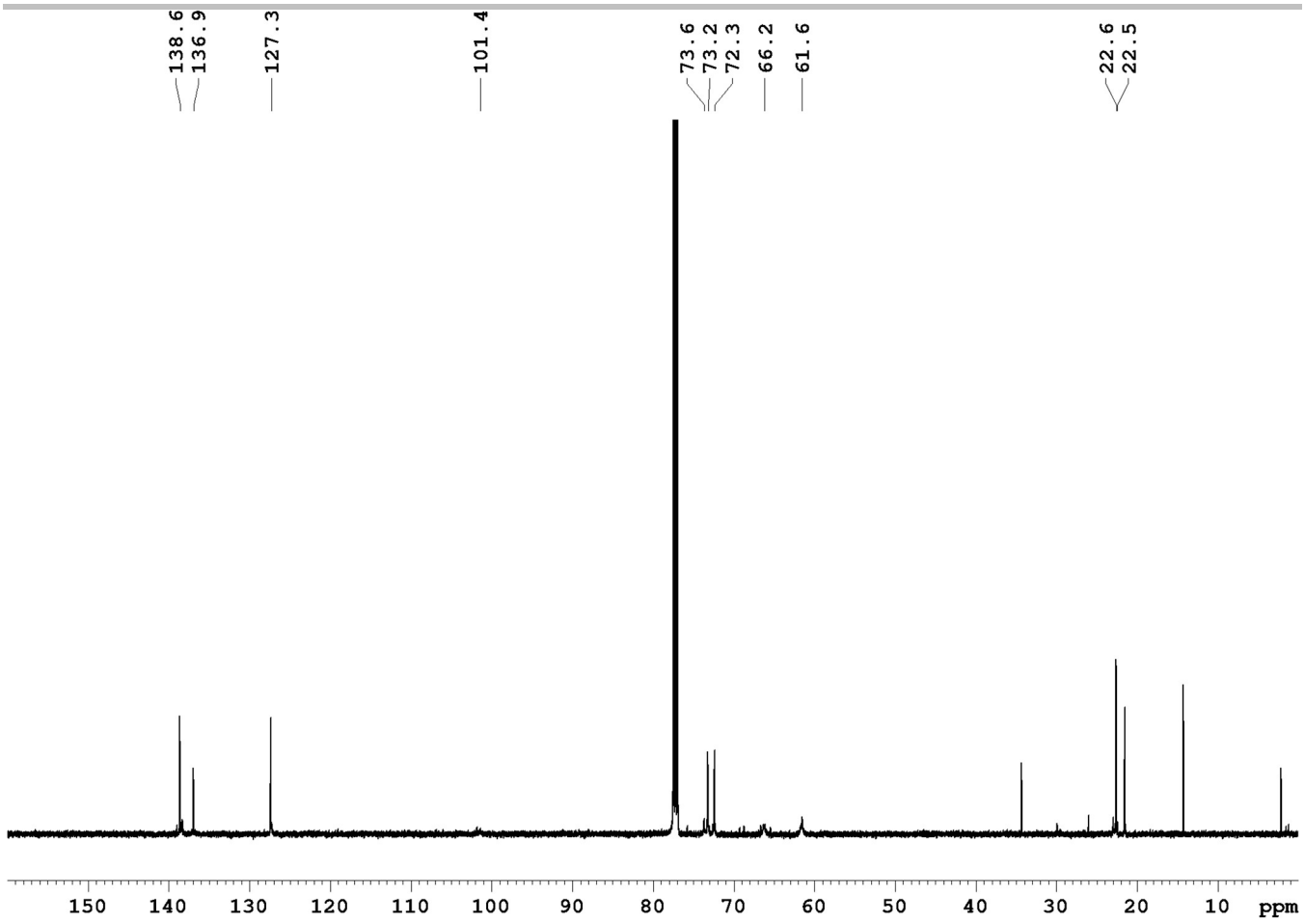



**Figure 18.** $^{13}C$ NMR spectrum of **8** (126 MHz, $CDCl_3$).

## Mass spectra

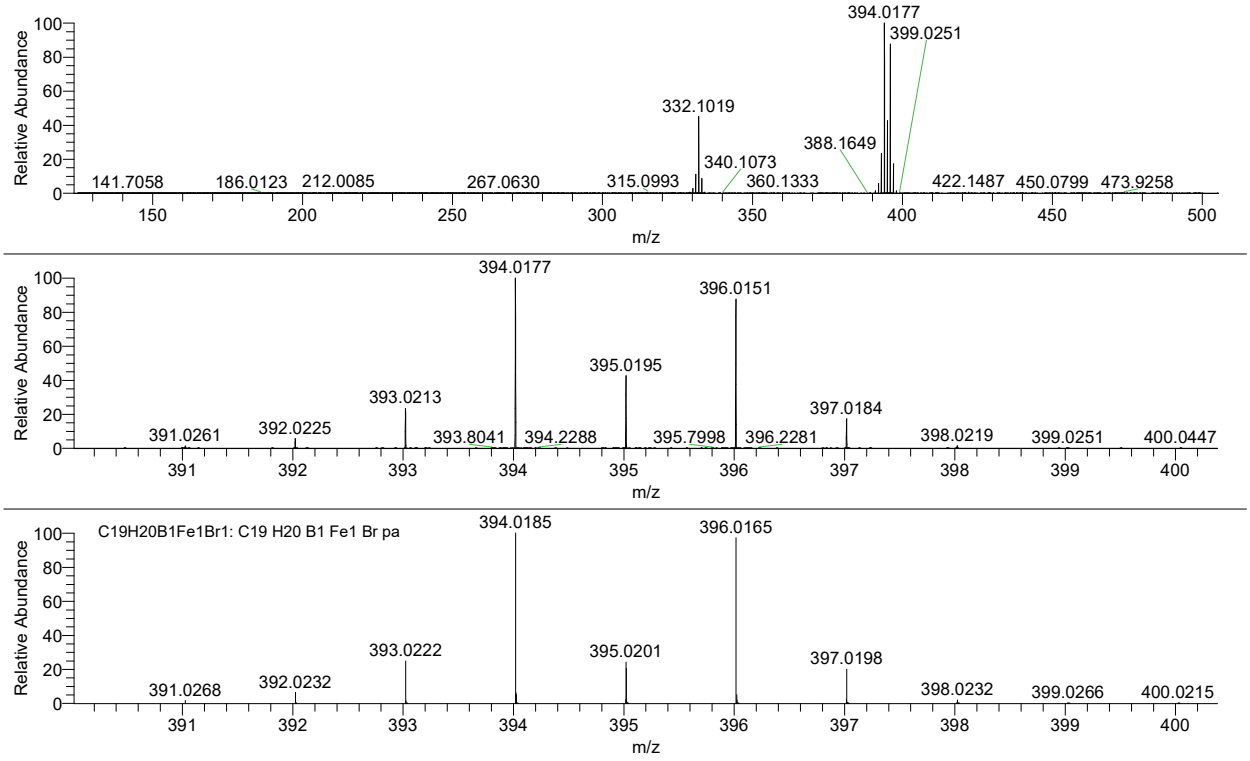



**Figure 19.** ACPI MS spectrum of **2**.

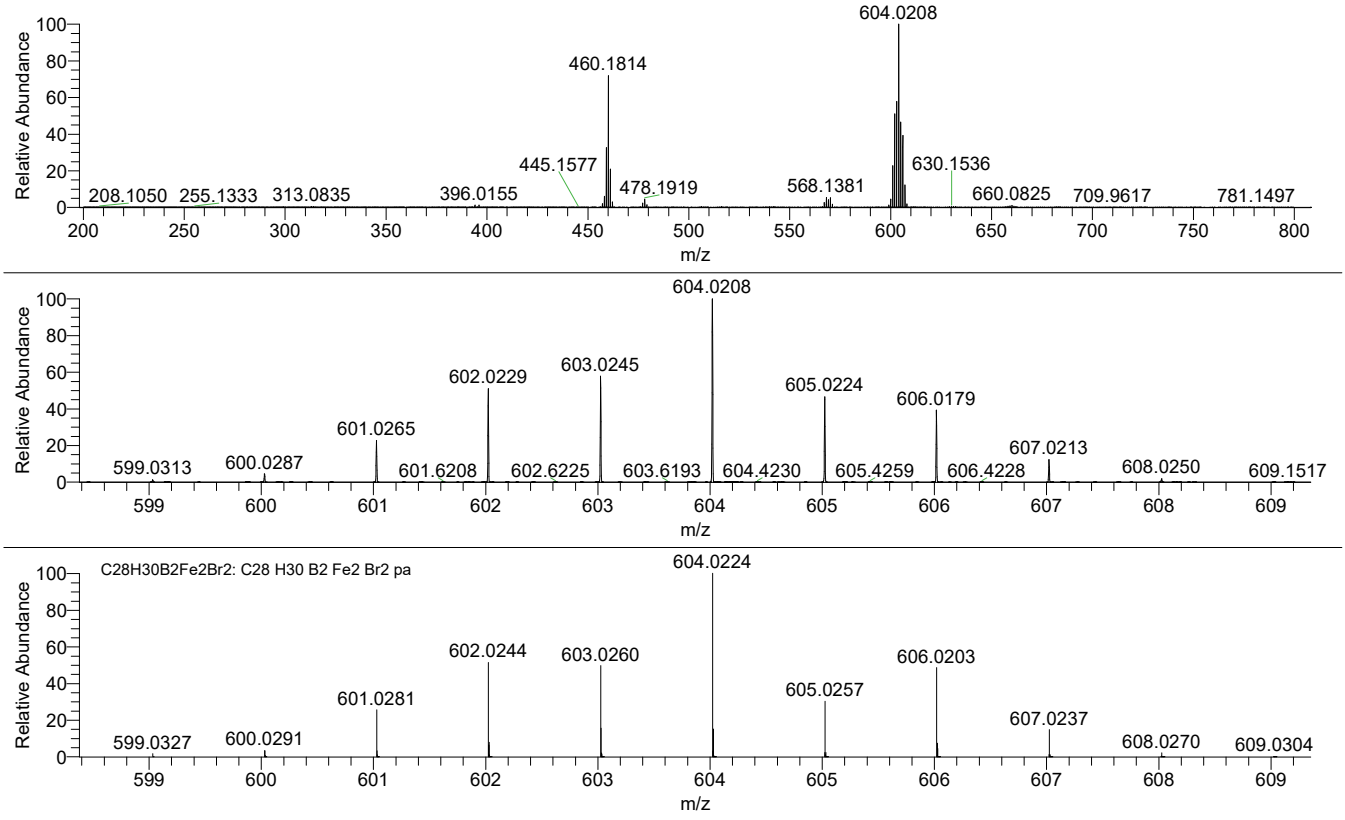



**Figure 20.** ACPI MS spectrum of **3**.

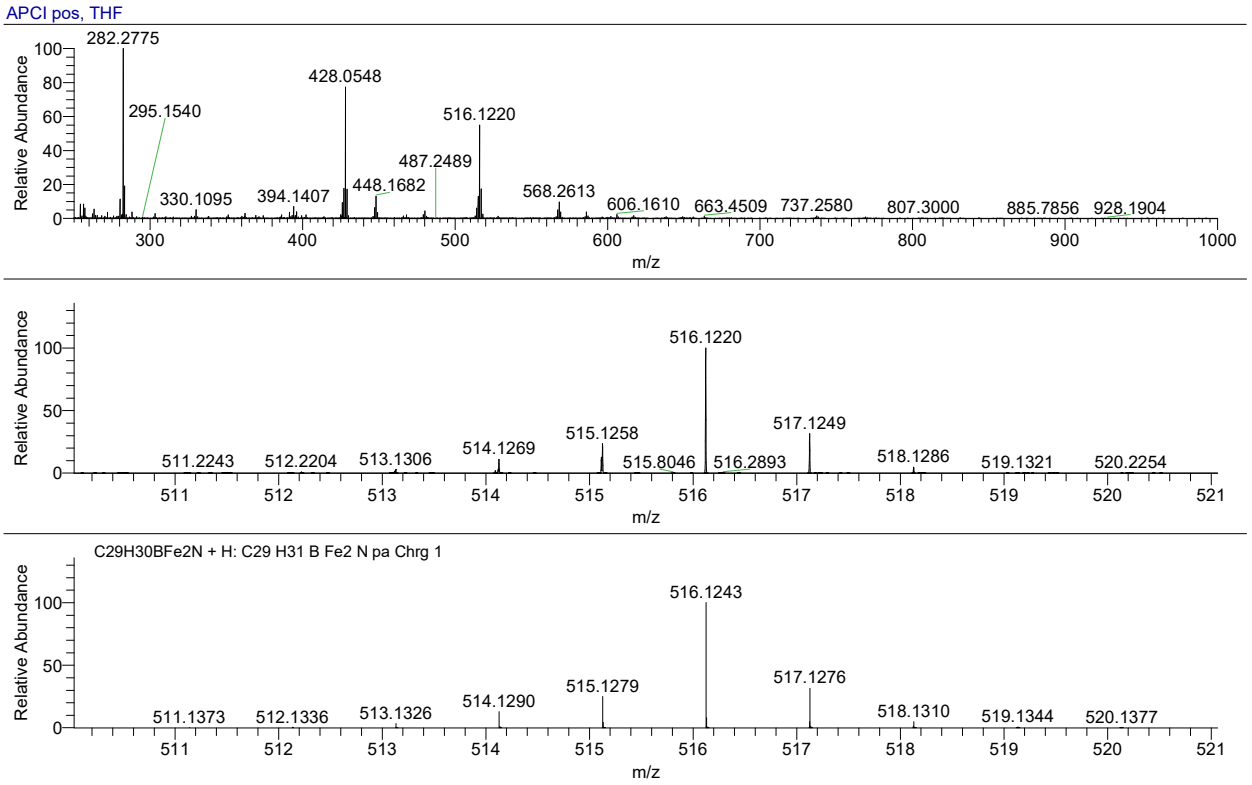



**Figure 21.** ACPI MS spectrum of **5**.

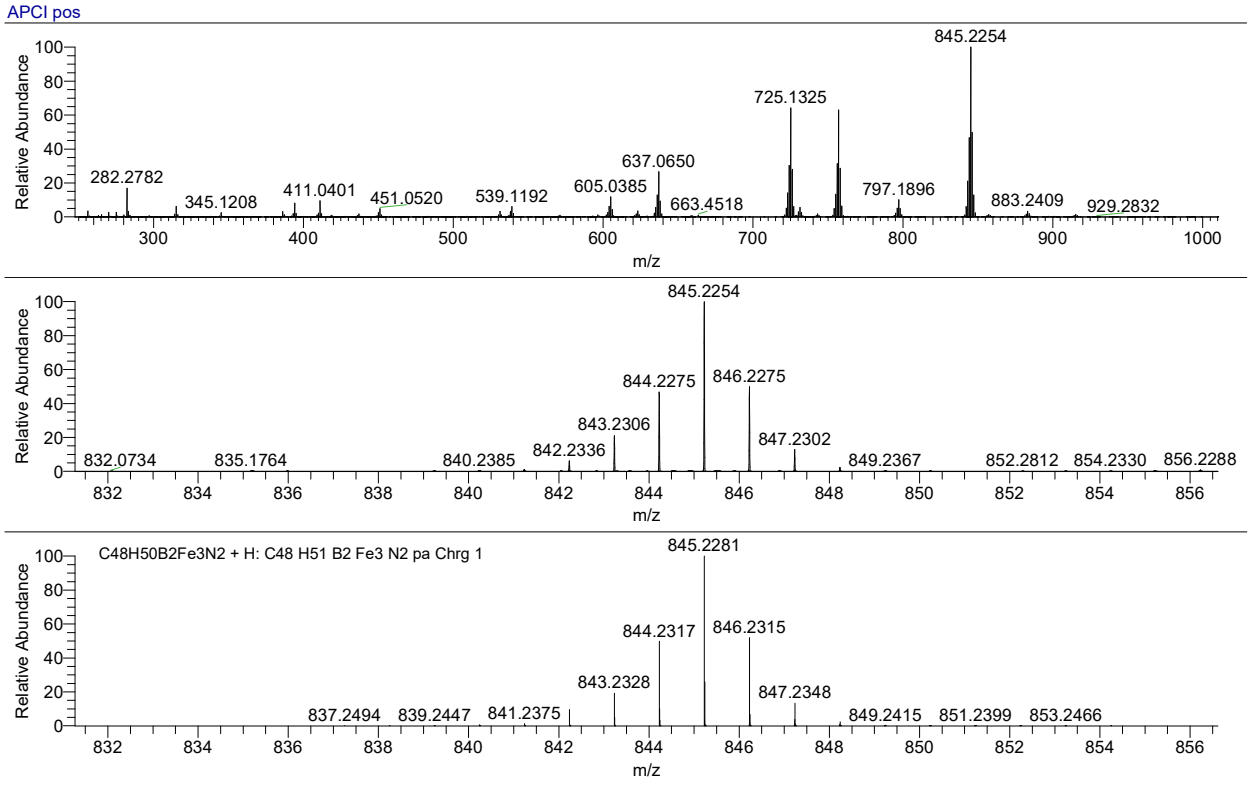



**Figure 22.** APCI MS spectrum of **6**.

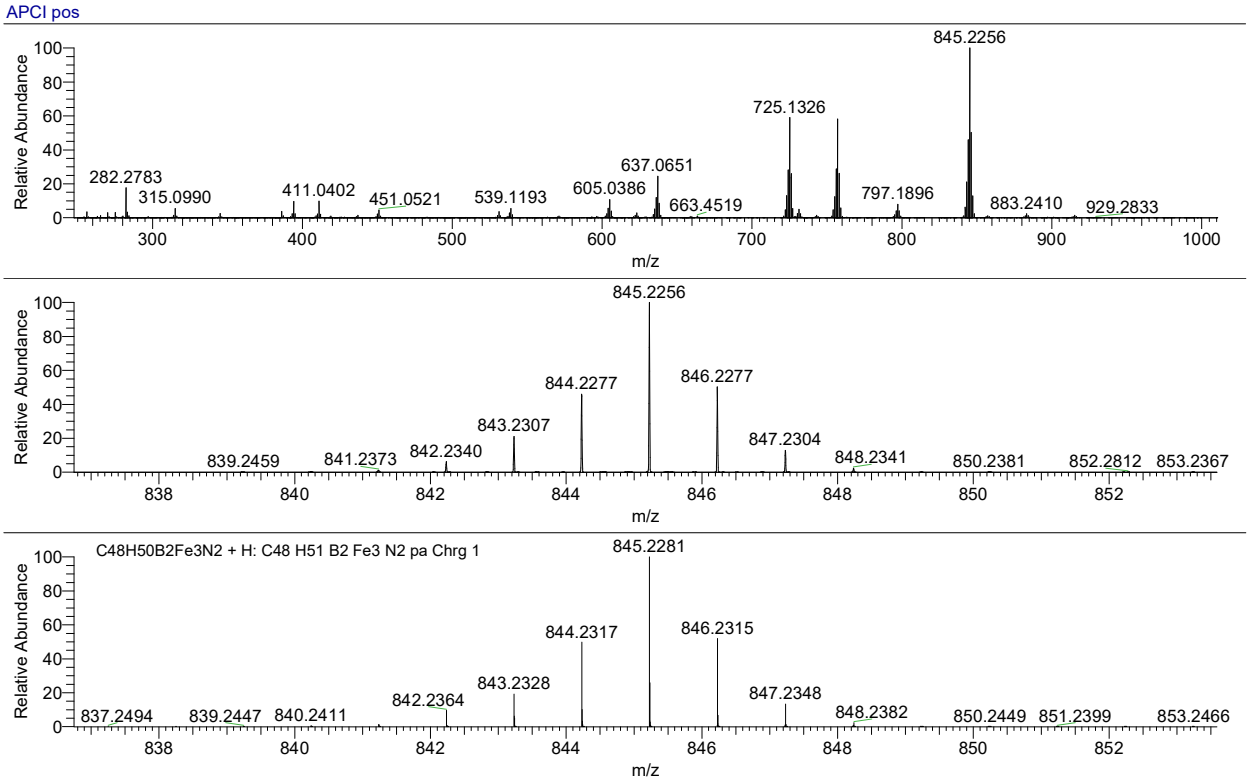



**Figure 23.** APCI MS spectrum of **7**.

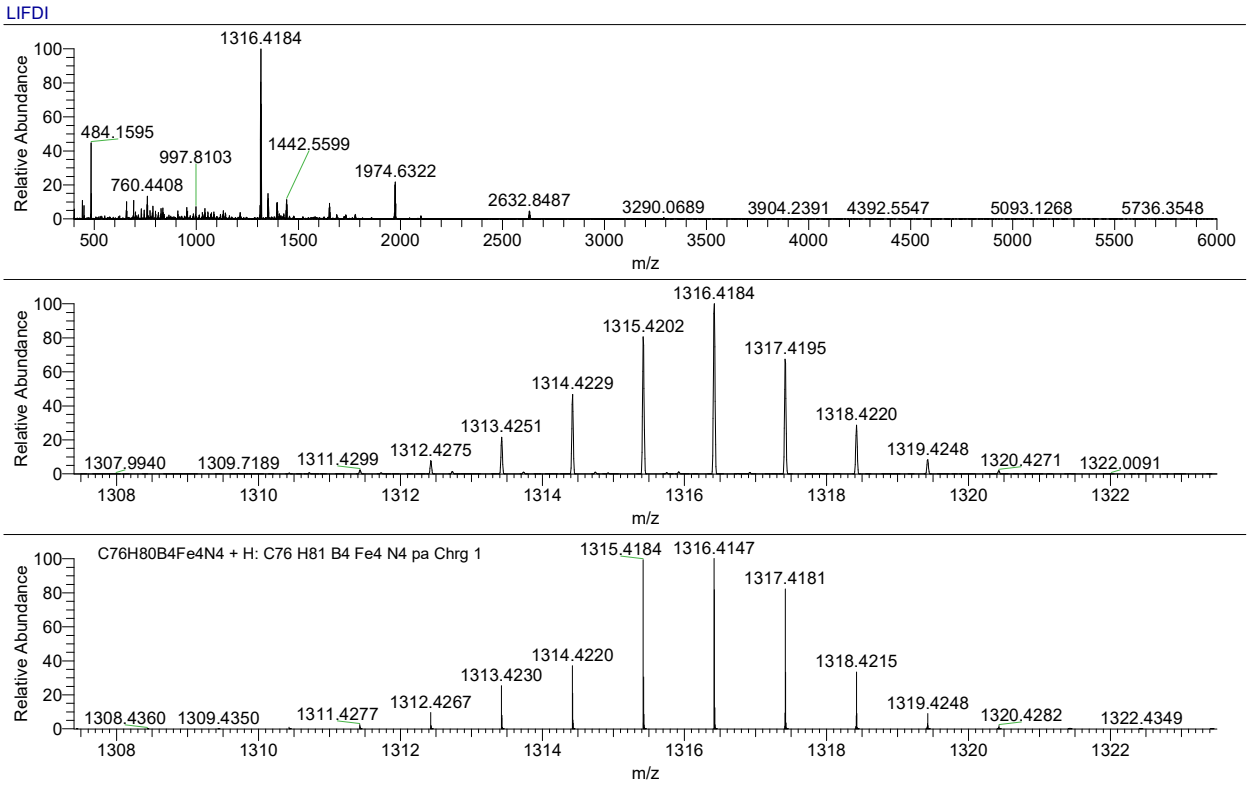



**Figure 24.** LIFDI MS spectrum of **8**.

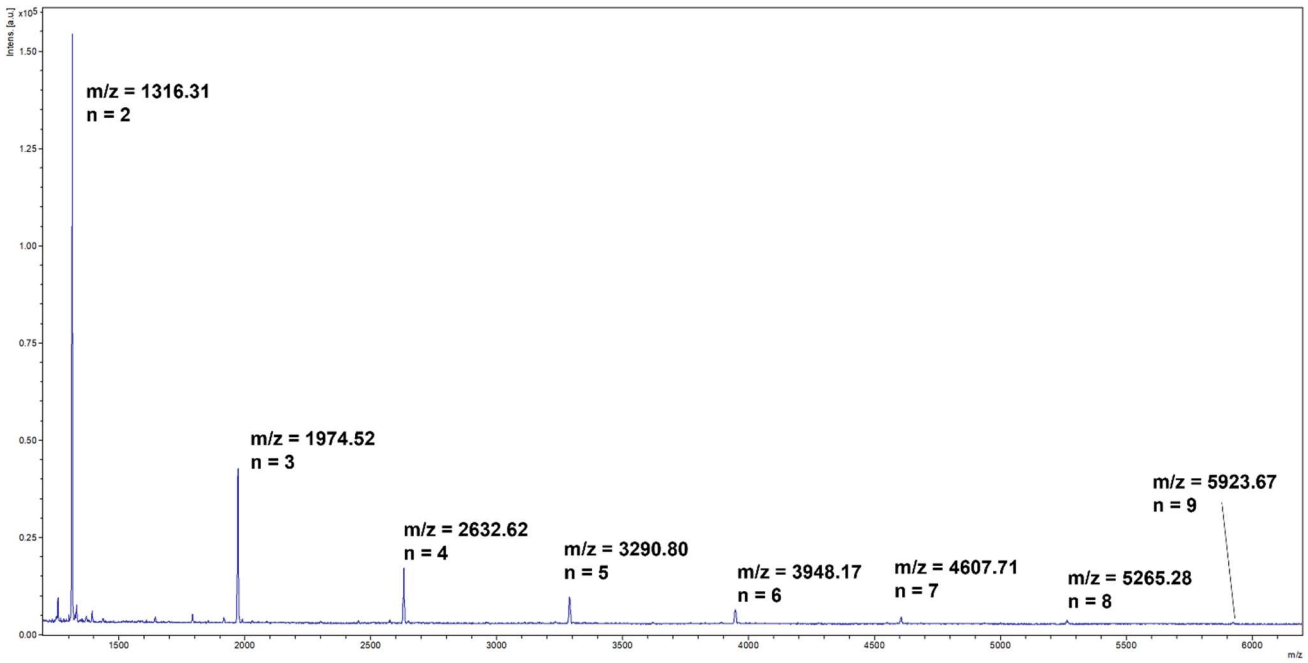



**Figure 25.** MALDI MS spectrum of **8**.

## Electrochemical studies

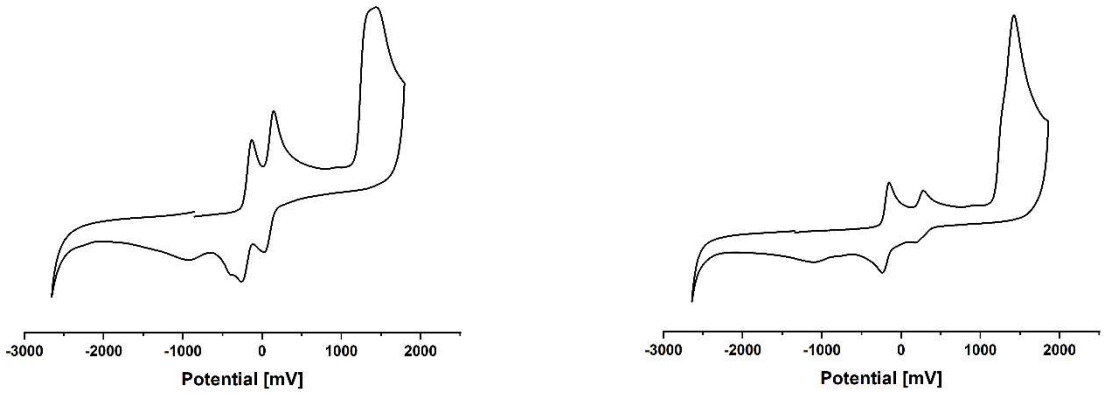



**Figure 26.** Cyclic voltammograms of **5** (left) and **6** (right) recorded in DCM containing 0.1 M [*n*-$Bu_4N$][$PF_6$] and referenced to $[Fc]^{0/+}$, scan rate: 250 mV $s^{-1}$.

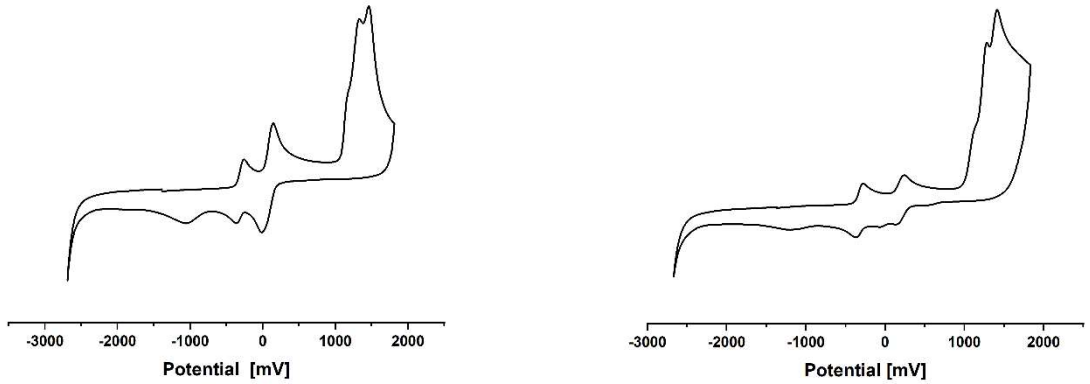



**Figure 27.** Cyclic voltammograms of **7** (left) and **8** (right) recorded in DCM containing 0.1 M [*n*-$Bu_4N$][$PF_6$] and referenced to $[Fc]^{0/+}$, scan rate: 250 mV $s^{-1}$.

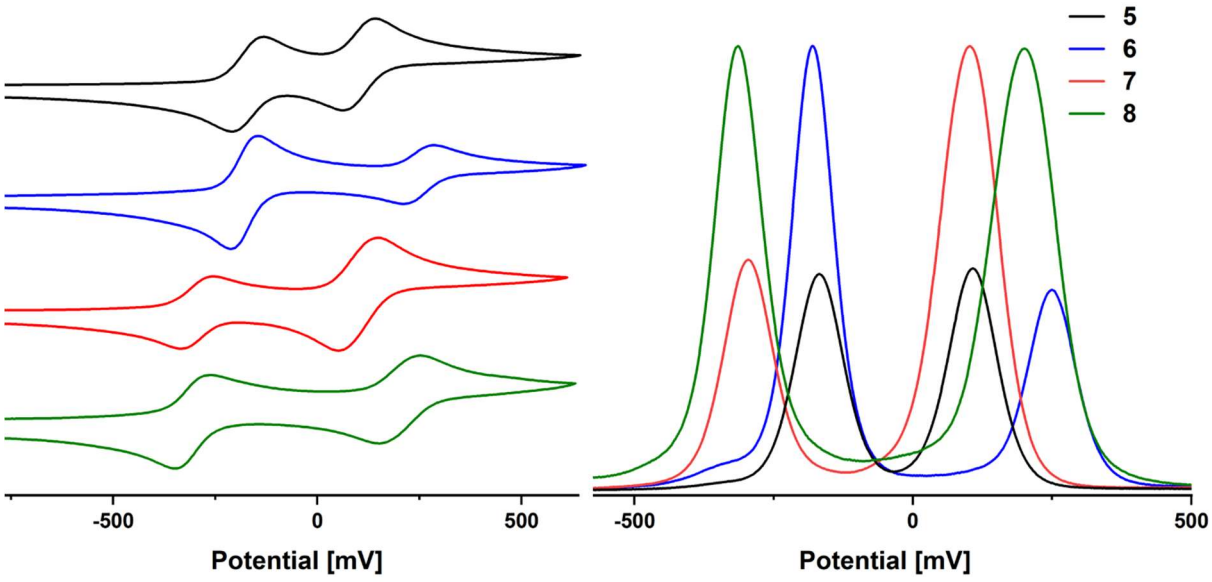



**Figure 28.** Cyclic voltammograms (left) and square wave voltammograms (right) of **5, 6, 7 and 8** recorded in DCM containing 0.1 M [*n*-$Bu_4N$][$PF_6$] and referenced to $[Fc]^{0/+}$, scan rate: 250 mV $s^{-1}$.

## GPC Traces

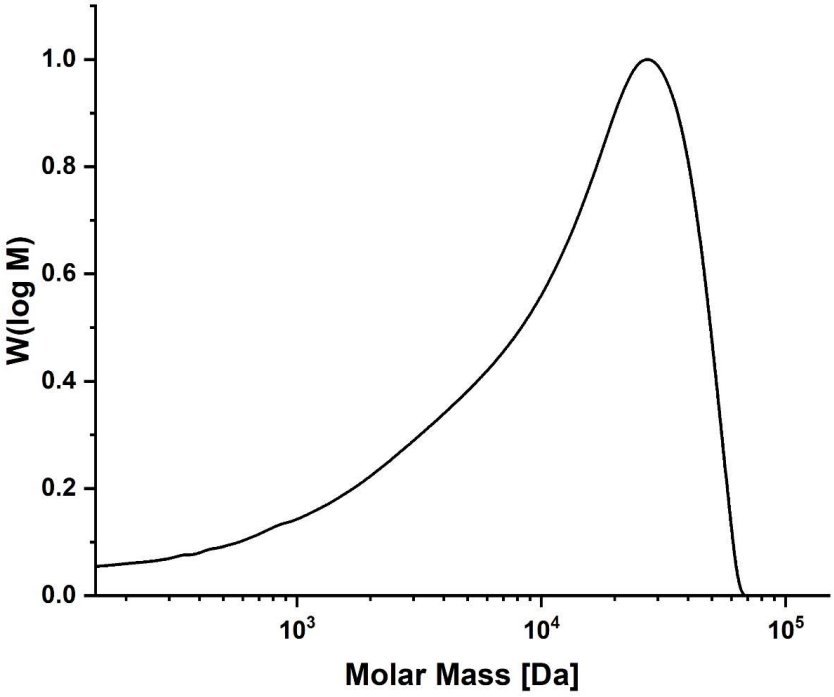



**Figure 29**. GPC trace of **8** (in THF, vs. polystyrene standard).

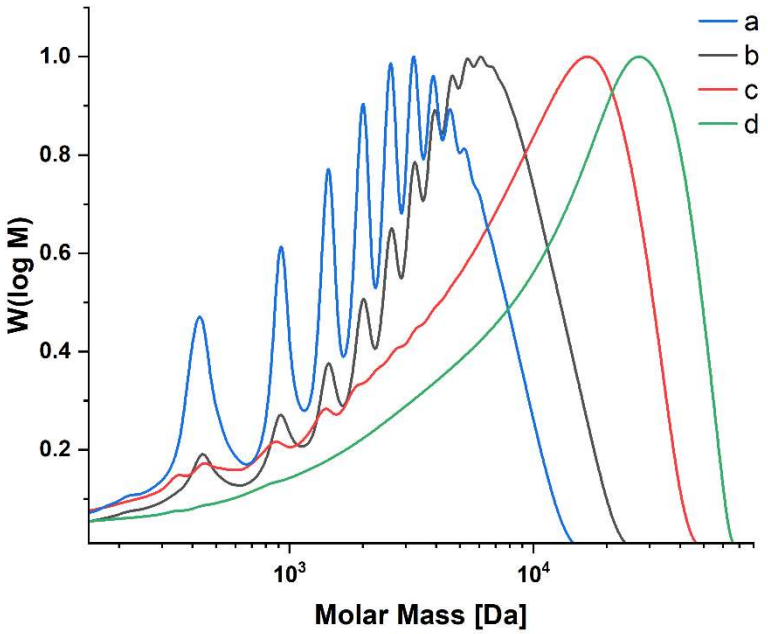
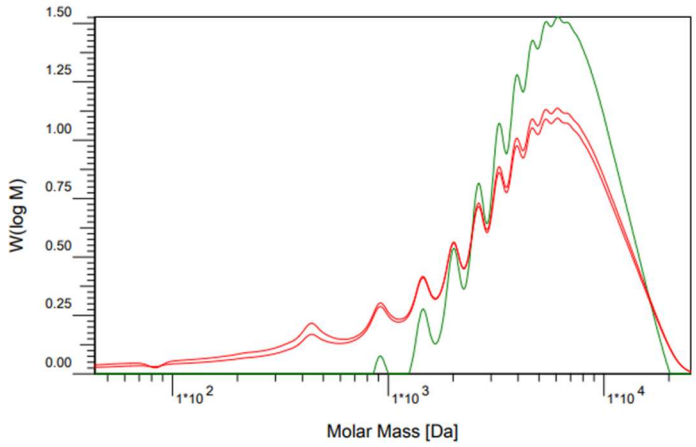
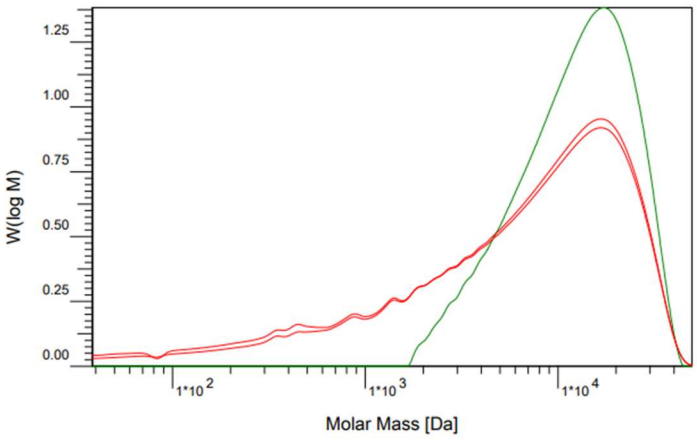



**Figure 30.** GPC traces of **8** for different reaction times: 1 d (a), 3 d (b), 5 d (c), 14 d (d) (in THF, vs. polystyrene standard).



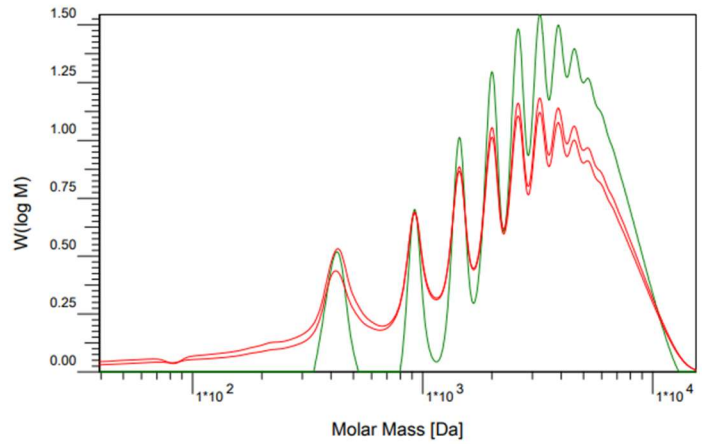

| | I1: RID 1, RI Signal | Unsicherheit [%] | I1: VWD 1, Signal A | Unsicherheit [%] | I1: VWD 1, Signal B | Unsicherheit [%] | |
|---|---|---|---|---|---|---|---|
| Mn : | 4.6736e3 | 15.40 | 1.1921e3 | 3.15 | 1.3960e3 | 2.46 | g/mol |
| Mw : | 6.4974e3 | 15.40 | 5.3600e3 | 3.14 | 5.5451e3 | 2.45 | g/mol |
| Mz : | 8.4643e3 | 15.40 | 8.8031e3 | 3.15 | 8.8416e3 | 2.46 | g/mol |
| Mv : | 0.000000 | 15.40 | 0.000000 | 3.15 | 0.000000 | 2.46 | g/mol |
| D : | 1.3902e0 | 21.77 | 4.4964e0 | 4.44 | 3.9722e0 | 3.47 | |
| [n]: | 0.000000 | 0.00 | 0.000000 | 0.00 | 0.000000 | 0.00 | ml/g |
| Vp : | 2.4380e1 | 15.40 | 2.4379e1 | 0.08 | 2.4379e1 | 0.02 | ml |
| Mp : | 6.1026e3 | 15.40 | 6.1034e3 | 3.15 | 6.1034e3 | 2.46 | g/mol |
| FI : | 1.3777e1 | 15.40 | 3.6529e3 | 0.08 | 2.4895e3 | 0.02 | ml*V |
| < 43 | 0.00 | 15.40 | 0.00 | 0.08 | 0.00 | 0.02 | |
| w% : | 100.00 | 15.40 | 100.00 | 0.08 | 100.00 | 0.02 | |
| > 25254 | 0.00 | 15.40 | 0.00 | 0.08 | 0.00 | 0.02 | |

**Figure 31.** Original GPC trace of **8** with a reaction time of 1 d (in THF, vs. polystyrene standard).



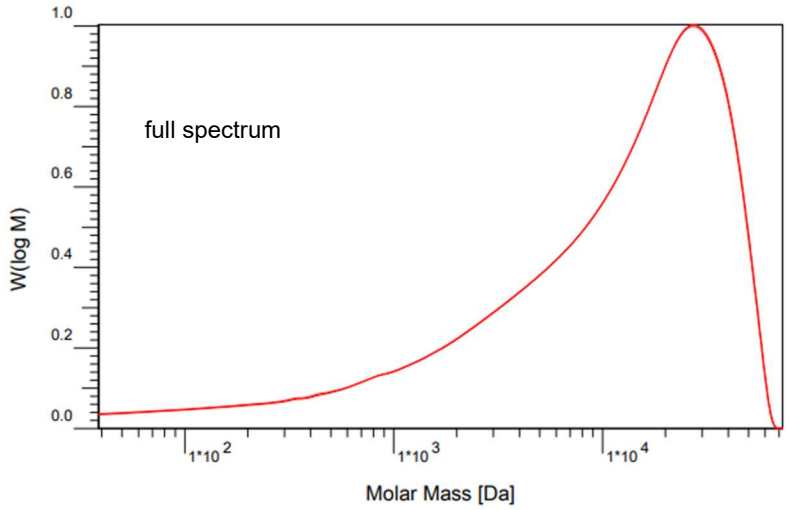

| | I1: RID 1, RI Signal | Unsicherheit [%] | I1: VWD 1, Signal A | Unsicherheit [%] | I1: VWD 1, Signal B | Unsicherheit [%] | |
|---|---|---|---|---|---|---|---|
| Mn : | 9.2527e3 | 6.62 | 1.1754e3 | 3.45 | 1.3949e3 | 2.77 | g/mol |
| Mw : | 1.4462e4 | 6.61 | 1.0475e4 | 3.45 | 1.0783e4 | 2.76 | g/mol |
| Mz : | 1.9422e4 | 6.62 | 1.8753e4 | 3.45 | 1.8747e4 | 2.77 | g/mol |
| Mv : | 0.000000 | 6.62 | 0.000000 | 3.45 | 0.000000 | 2.77 | g/mol |
| D : | 1.5630e0 | 9.35 | 8.9121e0 | 4.87 | 7.7302e0 | 3.91 | |
| [n]: | 0.000000 | 0.00 | 0.000000 | 0.00 | 0.000000 | 0.00 | ml/g |
| Vp : | 2.1771e1 | 6.61 | 2.1837e1 | 0.36 | 2.1837e1 | 0.11 | ml |
| Mp : | 1.7756e4 | 6.62 | 1.7272e4 | 3.45 | 1.7272e4 | 2.77 | g/mol |
| FI : | 1.2947e1 | 6.61 | 3.4947e3 | 0.36 | 2.3927e3 | 0.11 | ml*V |
| < 38 | 0.00 | 6.61 | 0.00 | 0.36 | 0.00 | 0.11 | |
| w% : | 100.00 | 6.61 | 100.00 | 0.36 | 100.00 | 0.11 | |
| > 49516 | 0.00 | 6.61 | 0.00 | 0.36 | 0.00 | 0.11 | |

**Figure 32.** Original GPC trace of **8** with a reaction time of 3 d (in THF, vs. polystyrene standard).



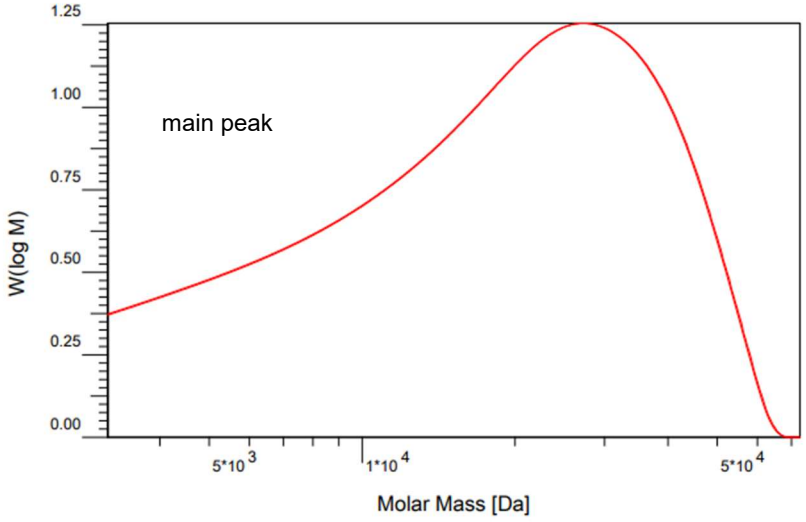

| | I1: RID 1, RI Signal | Unsicherheit [%] | I1: VWD 1, Signal A | Unsicherheit [%] | I1: VWD 1, Signal B | Unsicherheit [%] | |
|---|---|---|---|---|---|---|---|
| Mn : | 2.1644e3 | 9.58 | 8.2630e2 | 4.39 | 9.6818e2 | 3.44 | g/mol |
| Mw : | 3.8592e3 | 9.58 | 3.1673e3 | 4.39 | 3.3234e3 | 3.44 | g/mol |
| Mz : | 5.3300e3 | 9.58 | 5.3751e3 | 4.39 | 5.4226e3 | 3.44 | g/mol |
| Mv : | 0.000000 | 9.58 | 0.000000 | 4.39 | 0.000000 | 3.44 | g/mol |
| D : | 1.7830e0 | 13.54 | 3.8331e0 | 6.20 | 3.4326e0 | 4.86 | |
| [n]: | 0.000000 | 0.00 | 0.000000 | 0.00 | 0.000000 | 0.00 | ml/g |
| Vp : | 2.5938e1 | 9.58 | 2.5938e1 | 0.14 | 2.5938e1 | 0.24 | ml |
| Mp : | 3.2359e3 | 9.58 | 3.2363e3 | 4.39 | 3.2363e3 | 3.44 | g/mol |
| FI : | 1.3044e1 | 9.58 | 3.5091e3 | 0.14 | 2.3416e3 | 0.24 | ml*V |
| < 40 | 0.00 | 9.58 | 0.00 | 0.14 | 0.00 | 0.24 | |
| w% : | 100.00 | 9.58 | 100.00 | 0.14 | 100.00 | 0.24 | |
| > 15422 | 0.00 | 9.58 | 0.00 | 0.14 | 0.00 | 0.24 | |

**Figure 33.** Original GPC trace of **8** with a reaction time of 5 d (in THF, vs. polystyrene standard).




| | I1: VWD 1, Signal A | Unsicherheit [%] | I1: VWD 1, Signal B | Unsicherheit [%] | |
|---|---|---|---|---|---|
| Mn : | 1.5074e3 | 2.54 | 1.5581e3 | 2.45 | g/mol |
| Mw : | 1.7177e4 | 2.53 | 1.7330e4 | 2.44 | g/mol |
| Mz : | 2.9482e4 | 2.54 | 2.9641e4 | 2.44 | g/mol |
| Mv : | 0.000000 | 2.54 | 0.000000 | 2.45 | g/mol |
| D : | 1.1396e1 | 3.58 | 1.1122e1 | 3.45 | |
| [n]: | 0.000000 | 0.00 | 0.000000 | 0.00 | ml/g |
| Vp : | 2.0566e1 | 0.00 | 2.0549e1 | 0.00 | ml |
| Mp : | 2.9932e4 | 2.55 | 3.0160e4 | 2.45 | g/mol |
| FI : | 2.9158e3 | 0.00 | 2.0690e3 | 0.00 | ml*V |
| < 38 | 0.00 | 0.00 | 0.00 | 0.00 | |
| w% : | 100.00 | 0.00 | 100.00 | 0.00 | |
| > 72737 | 0.00 | 0.00 | 0.00 | 0.00 | |

**Figure 34.** Original GPC trace of **8** with a reaction time of 14 d (in THF, vs. polystyrene standard).




| | I1: VWD 1, Signal A | Unsicherheit [%] | I1: VWD 1, Signal B | Unsicherheit [%] | |
|---|---|---|---|---|---|
| Mn : | 1.2454e4 | 0.21 | 1.2504e4 | 0.21 | g/mol |
| Mw : | 2.1236e4 | 0.09 | 2.1344e4 | 0.09 | g/mol |
| Mz : | 2.9890e4 | 0.19 | 3.0045e4 | 0.19 | g/mol |
| Mv : | 0.000000 | 0.21 | 0.000000 | 0.21 | g/mol |
| D : | 1.7052e0 | 0.22 | 1.7070e0 | 0.22 | |
| [n]: | 0.000000 | 0.00 | 0.000000 | 0.00 | ml/g |
| Vp : | 2.0566e1 | 0.00 | 2.0549e1 | 0.00 | ml |
| Mp : | 2.9932e4 | 0.25 | 3.0160e4 | 0.25 | g/mol |
| FI : | 2.3241e3 | 0.00 | 1.6558e3 | 0.00 | ml*V |
| < 3155 | 0.00 | 0.00 | 0.00 | 0.00 | |
| w% : | 100.00 | 0.00 | 100.00 | 0.00 | |
| > 72737 | 0.00 | 0.00 | 0.00 | 0.00 | |

**Figure 35.** Section of the original GPC trace of **8** with a reaction time of 14 d (in THF, vs. polystyrene standard).

## X-Ray-Crystallography

Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-Kα radiation. The crystals were cooled using an Oxford Cryostreams low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)[7] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against $F^2$ of all data, using SHELXL[8] software and the SHELXLE graphical user interface.[9]

**Table 1. Single-crystal X-ray diffraction data and structure refinements of 5, 6 and 7.**

| Compound | **5** | **6** | **7** |
|---|---|---|---|
| CCDC number | 2277969 | 2277970 | 2277971 |
| Size / mm³ | 0.300 x 0.501 x 0.816 | 0.154 x 0.282 x 0.354 | 0.168 x 0.243 x 0.356 |
| Empirical formula | $C_{29}H_{30}BFe_2N$ | $C_{48}H_{50}B_2Fe_3N_2$ | $C_{48}H_{50}B_2Fe_3N_2$ |
| $M$ / g mol$^{-1}$ | 515.05 | 844.07 | 844.07 |
| Crystal system | triclinic | monoclinic | triclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| $a$ / Å | 7.5682(16) | 21.066(11) | 7.4462(12) |
| $b$ / Å | 11.052(4) | 7.861(4) | 10.701(2) |
| $c$ / Å | 14.463(5) | 24.097(13) | 13.3227(19) |
| $\alpha$ / ° | 82.913(17) | 90 | 74.359(6) |
| $\beta$ / ° | 86.11(2) | 95.11(3) | 86.801(6) |
| $\gamma$ / ° | 78.996(11) | 90 | 76.243(6) |
| $V$ / Å$^3$ | 1177.2(6) | 3975(3) | 992.9(3) |
| $Z$ | 2 | 4 | 1 |
| $\rho_{calc}$ / g cm$^{-3}$ | 1.453 | 1.411 | 1.412 |
| $\mu$ / mm$^{-1}$ | 1.250 | 1.118 | 1.118 |
| $T$ / K | 100(2) | 100(2) | 100(2) |
| $\theta_{min,max}$ / ° | 1.420, 26.436 | 1.231, 26.022 | 2.032, 26.462 |
| Completeness | 0.997 | 0.999 | 0.987 |
| Reflections: collected / unique | 26437 / 4580 | 57228 / 7838 | 26488 / 4064 |
| $R_{int}$ | 0.0497 | 0.0919 | 0.0291 |
| R1 [I>2σ(I)] | 0.0308 | 0.0836 | 0.0323 |
| $wR_2$ (all data) | 0.0820 | 0.2121 | 0.0785 |
| Max. / min. residual electron density / e Å$^{-3}$ | 0.497 / −0.365 | 1.251 / −0.885 | 0.494 / −0.292 |

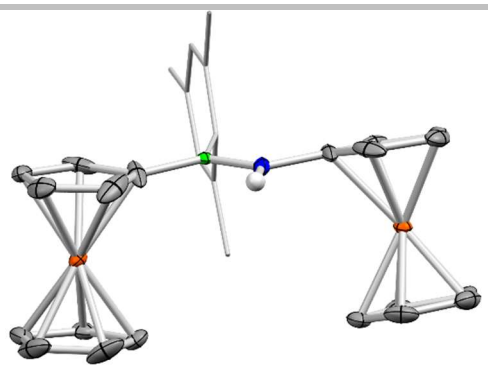


**Figure 36.** Solid-state molecular structure of **5**. (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bounded H have been omitted for clarity). The B and N positions of **5** are disordered and only one part (52% occupancy) is shown here.

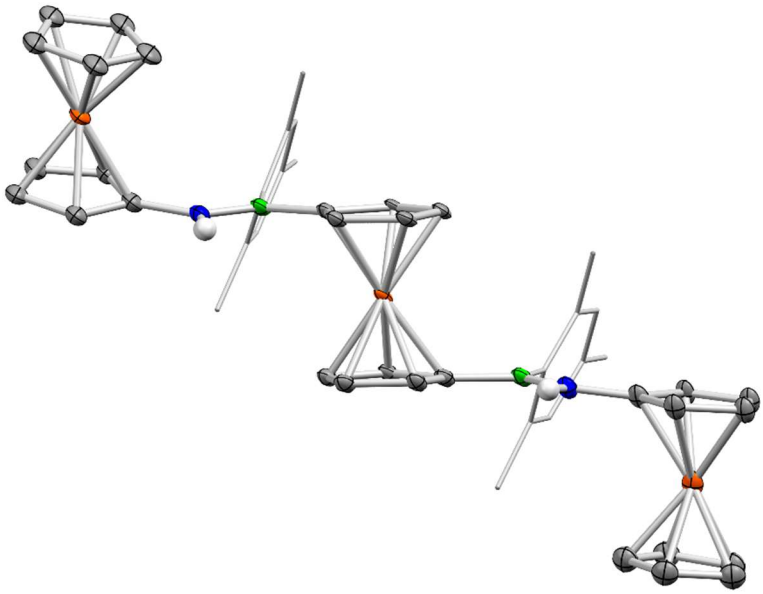


**Figure 37.** Solid-state molecular structure of **6**. (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bounded H have been omitted for clarity).

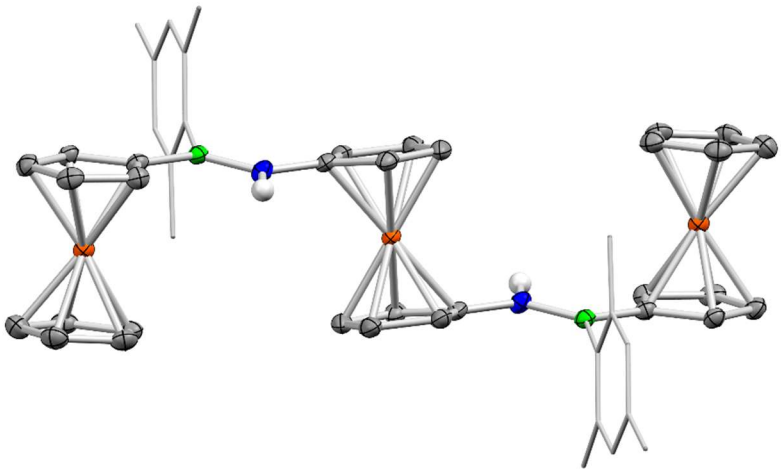


**Figure 38.** Solid-state molecular structure of **7**. (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bounded H have been omitted for clarity).

## References


[1] A. Appel, H. Nöth and M. Schmidt, *Chem. Ber.,* 1995, ***128***, 621.
[2] K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer and P. P. Power, *J. Am. Chem. Soc.,* 1993, ***115***, 11353.
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[5] F. Jäkle and I. Manners, *Organometallics,* 1999, ***18***, 2628.
[6] a) M. Scheibitz, J. B. Heilmann, R. F. Winter, M. Bolte, J. W. Bats and M. Wagner, *Dalton Trans.,* 2005, **159**; b) M. Karas, M. Glückmann and J. Schäfer, *J. Mass Spectrom.,* 2000, ***35***, 1; c) R. Zenobi and R. Knochenmuss, *Mass Spectrom. Rev.,* 1998, ***17***, 337.
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[8] G. M. Sheldrick, *Acta Crystallogr.,* 2008, ***64,*** 112.
[9] C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.,* 2011, ***44***, 1281.